

Fabrication of Si nanowire/microwire solar cells for the realization of cost-effective nanostructured silicon solar cells.

A dissertation

submitted in partial fulfilment of the requirements for the degree of

INTEGRATED MASTER OF TECHNOLOGY

IN

ENERGY ENGINEERING

By

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CUJ/I/2014/IEE/006



DEPARTMENT OF ENERGY ENGINEERING

CENTRAL UNIVERSITY OF JHARKHAND

MAY 2019



Central University of Jharkhand

(Established by Act of Parliament of India, 2009)

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Certificate of Approval

The foregoing thesis by **Miss Shrestha Bhattacharya** Regn. No.CUJ/I/2014/TEE/006is hereby approved as a creditable study carried out and presented in a manner satisfactory to warrant its acceptance as a pre-requisite to the degree for which it has been submitted. It is understood that by this approval the under signed do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve only for the purpose for which it is submitted.

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Acknowledgement

I am deeply indebted to Dr. Sanjay k. Srivastava (Senior Scientist CSIR-NPL) and Dr. Mrinal Dutta (Ramanujan Fellow CSIR-NPL) for their expert guidance and constant encouragement throughout the period of my project. I am grateful for their motivation, patience and precious time that they had devoted to my project work. It has truly been a wonderful experience to work under their able guidance.

I am also thankful to the honorable director of CSIR-NPL, group head Mr. C.M.S. Rauthan and all other scientists Dr. P. Pratap, Dr. Vandana and research colleagues at NPL for their advice and friendly support in a new environment. I am also very thankful to my seniors for their constructive feedback and evaluation which helped me a lot to achieve my goals in this project. I would like to make a special thanks to my colleges and Department, Prof S.K. Samdharshi, Dr. Bishnu Mohan Jha, Dr. Basudev Pradhan and P.S. Panja and all other faculty members for their recommendation and much needed motivation to work in CSIR-NPL.

Most importantly, I express my heartfelt gratitude to my labmates for being limitlessly supporting me especially Avritti di, Meenakshi di, Aishik, Shweta maam, Nitin, Pragya Di, Veenu Di for their help whenever it was required. I express all my respect and love to Avritti di, Surajit da, Mrinal Sir, Subhajit da for letting me feel home that too kilometers away from home and sharing their knowledge. I also thank my companions Aishik and Indranil for supporting me always and to all other friends for sharing their smile with me. Last but not the least I would like to thank my parents for providing me mental as well as financial support and motivation to work and stay in an unknown atmosphere.

Shrestha Bhattacharya

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Abbreviations

a-Si	Amorphous Silicon
DSSC	Dye sensitized solar cells
FF	Fill Factor
PCE	Power Conversion Efficiency
AM	Air mass
SiNW	Silicon nano wire
SiMW	Silicon microwire
MCEE	Metal Catalyzed Electroless Etching
SEM	Scanning Electron microscope
QE	Quantum Efficiency
TEOS	Tetraethyl orthosilicate
KCl	Potassium Chloride

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Abstract

Si solar cells with radial junction nanowire (NW) arrays have attracted much attention in the recent years because of its potential in solving the problems faced by bulk Si solar cells. The main advantage of such kind of solar cells is that they exhibit higher absorbance for a given thickness than commercial Si solar cells due to incident light trapping within the NW arrays and offer the opportunity to use lower-grade Si wafers to produce efficient solar cells, due to the decoupling of charge carrier collection and light absorption directions, thus enabling lower-cost solar cell production. However, production of radial p-n junction by conventional techniques fully depleted SiNWs sometime change the polarity of the NWs. The main reason of this is the small diameter of the SiNWs fabricated by simple and low-cost metal catalyzed electroless etching (MCEE) technique. This project has been designed to understand the problem and solve this issue by synthesizing Si wires with large diameters. Using the MCEE technique SiNW arrays have been fabricated on p- Si (100) substrates with resistivity 5-10 ohm-cm. The morphology and reflectance property of these NW arrays have been studied. The diameter of vertically aligned SiNWs, were found in the range of 40-200nm. The length of the Si NWs was controlled by changing the reaction time. Remarkable decrease in reflectivity (nearly 2-4% in 400-800 nm range) has been observed in SiNW array samples compared to the polished silicon surface. To fabricate Si microwire (SiMW) nanosphere lithography with MCEE technique has been used. A monolayer of self- assembled SiO₂ micro particles was formed on Si substrates and then size reduction is done using reactive ion etching. Then SiMW arrays were fabricated by depositing metal film on these self-assembled micro particles and then MCEE technique has been used.

This thesis has been divided into 5 chapters which are as follows:

Chapter 1: This chapter contains the introduction of renewable power, history of solar cells, introduction to solar cell mechanism, parameters, different losses in solar cells and also a short introduction to the SiNW and SiMW arrays.

Chapter 2: This chapter provides introduction to the different characterization techniques and their mechanism that are used to carry out the dissertation work.

Chapter 3: This chapter focuses on the fabrication of SiNW array solar cells and effect of NW length, surface defects and light trapping properties on the photovoltaic performance.

Chapter 4: This chapter emphasizes on the experimental technique for the synthesis of SiO₂

microparticles to make self-assembled single monolayer on Si substrates required for nanosphere lithography process.

Chapter 5: This chapter presents the research work carried out to fabricate SiMW arrays by nanosphere lithography technique in addition to MCEE technique. Also this chapter presents SiMW solar cell fabrication process and the advantage of SiMW solar cells over SiNW array solar cells prepared under identical conditions.

Chapter 1

1.Introduction

Human activities like deforestation, increased industrial growth has led to a considerable increase in the greenhouse gases in the atmosphere. These greenhouse gases mostly include carbon di-oxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, Sulphur fluoride etc. This leads to entrapment of insolation in the atmosphere causing an increase in the earth's global average temperature by $\sim 1^{\circ}\text{C}$ over the period 1885-2016. This gradual heating of Earth's atmosphere and surface called global warming cause rise in the sea level, increase in the oceanic temperature leading to the migration of fishes to higher latitudes, acidification of ocean leading to coral bleaching and also various adverse effects on human and animal health[1-4]. These disastrous changes are mainly due to consumption of fossil fuels that burn to emit greenhouse gases as their byproducts. The natural fossil fuels are also much expensive and are depleting at a much faster rate, this increases the demand of the alternative renewable clean energy sources in the next few decades. Thus being depleted, these fossil fuel usages also have problematic long term consequences [5-11]. Among various energy sources that are present on the earth including hydroelectricity, biomass, wind and geothermal energy sunlight is the most abundant and easily available natural energy resource. In the last few decades, it has been seen that the consumption of energy around the globe has accelerated world energy demand by more than double [12]. It has been seen that world's four-fifth of the energy that is consumed comes from fossil fuel combustion which results in the 5.8% of the CO_2 emission in the atmosphere. At present, 19% of global energy consumption is shared by the renewable energy and it will continue to grow strongly in coming years [13]. We can say that the renewable energy technologies will offer long term sustainable solutions. In India almost most of the parts receive good solar radiation 4- 7 kWh/sq. m/day. There in some parts of our country there is also a good potential for wind as well about $>200\text{W/sq. m}$. There is also biomass and waste availability too. These renewables thus helped in meeting the growing energy demands and also provide clean energy by reducing the carbon footprints.

The Renewable Power Potential

Many renewable sources of energy were unable to satisfy human such as hydroelectric and nuclear due to most understandable safety problems. Thus solar energy is considered as a mature and reliable source of energy among all other renewable sources of energy. Solar energy technologies are quite easy to be installed in both industrial, household and individual level and

Table 1.1: shown below the approximate renewable energy that is installed latest

Resource	Estimated Potential (MW)	Installed Capacity as on 31.12.2018
Wind	> 102,000	35138.15
Solar	30-50 MW/ sq. km	23858.13 1354.12
Small Hydro (up to 25 MW)	20,000	4517.45
Bioenergy -Power	22,000	9780.24
Waste to Power	4,000	138.30
Geothermal & Tidal etc.	20,000	-
Total	Solar + >1,68,000	74786.390

does not require much infrastructural cost. It only requires some technological capability to harness it. This technology is mainly divided into two types- active and passive technologies. In active, it converts sun's energy from heat to other useful form such as electricity and hot water. It involves solar thermal collector and solar photovoltaic (PV) devices. In passive technologies direct use of solar energy for home heating. The designing of a building in such a way that it efficiently harvests and stores the sun energy in the building is best example of passive heating. Photovoltaic refers to the conversion of sunlight into electricity directly.

1.1History of Solar Cells

As we know that solar power is no more than 60 years old, but the discoveries that led to the solar cell began nearly 200 years ago. New discoveries with time about the properties of light and conductivity have made solar power what it is today. The photovoltaic (PV) effect was first observed by Edmund Becquerel way back in 1839. He observed that when exposed to light source platinum electrode immersed in an electrolyte produced an electric current [14]. In 1873-1876, selenium's photoconductivity was discovered

by Willoughby Smith that means it becomes electrically conductive when it absorbs light. After three years, William Grylls Adams and Richard Evans Day learned that selenium could produce electricity from light without heat. This discovery proved that solar power is easy to maintain and harvest. Later in 1883 Charles Fritts created the first solar cell by coating selenium with a thin layer of gold which achieved an energy conversion rate of 1–2%. In 1887, German physicist Heinrich Hertz first observed the photoelectric effect in which light strikes the solid surface to free electrons to produce power. Hertz found that in this process more power was produced when exposed to ultraviolet light. Later Albert Einstein received the Nobel Prize for further explaining this effect. Goldman and Brodsky further discovered in 1914 that the photoelectric effects so far were the result of the barrier to current flow in one of the semiconductor interfaces and in 1930 this idea was further developed by Walter Schottky [14].

In 1953-1956, the first Si solar cells were commercially produced. Physicist at Bell laboratories found that Si was more efficient than selenium and it was the first practical solar cell that was developed. This solar cell was capable of powering electrical devices and had a efficiency of about 6%. But at that time Si PV technology was not encouraged much due to the high cost of Si solar cells. Many experiments were carried out to increase the efficiency and for its commercialization.

In 1970 as the oil price increased, the demand for the solar energy increased. Exxon Corporation motivated and funded for research work to develop solar cells made from lower-grade Si and cheaper materials. This pushed the costs from \$100 per watt to only \$20–\$40 per watt. Several solar-friendly bills and initiatives were passed by the federal government and the National Renewable Energy Laboratory (NREL) was formed in 1977.

Earlier solar cells were made from Czochralski grown monocrystalline Si [15-16] and this material till date is used as a dominant material for solar cell because it is second most abundant material, non-toxic and a reliable as well as mature technology.

The interest for photovoltaics is increasing day by day and by 2008 PV production increased by 80% on the previous year with thin film devices accounting for 12-14% of the market share. With time many advancements took place which includes the first thin film devices in the late 1970s, multi-junction devices in the 1980s and organic devices in the 1990s [17]. The increased efficiencies of the various types of PV cells are shown below in Figure 1.1.

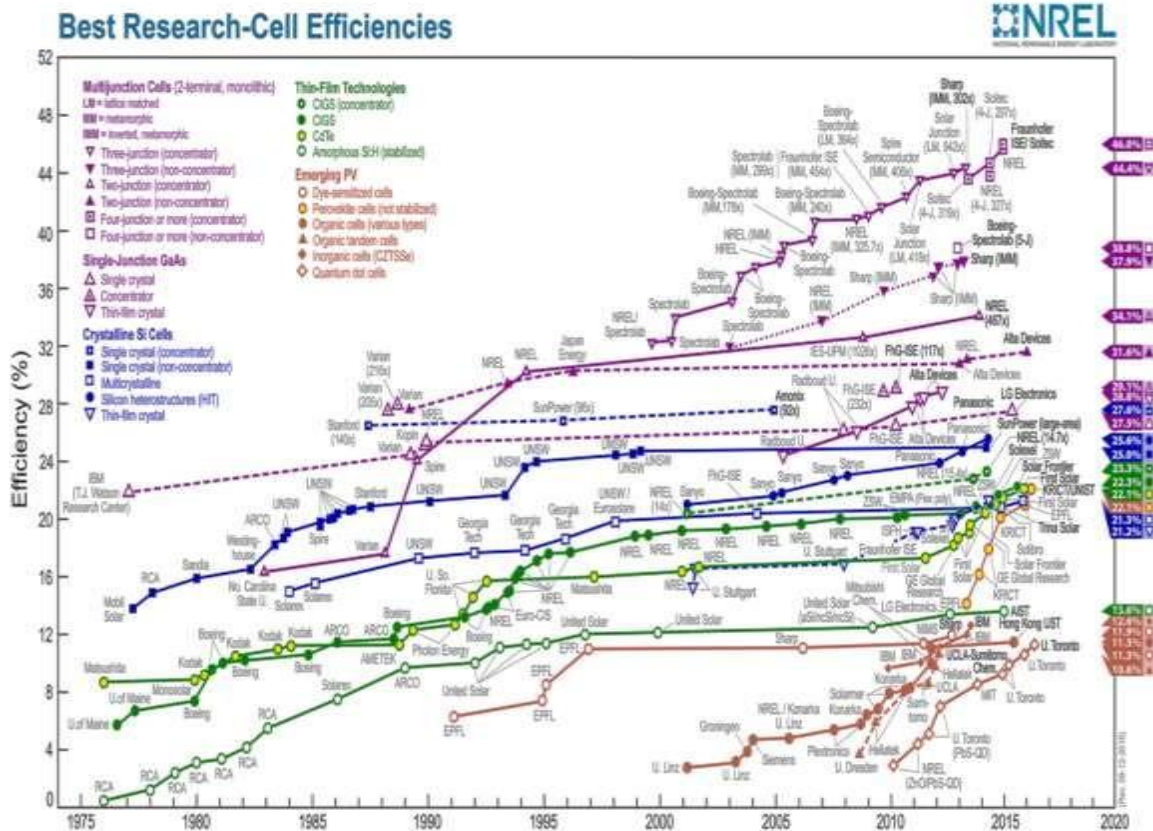


Figure 1.1 Improvements in solar cell efficiencies by type over time [18]

It can be seen that Si dominates as the primary materials for PV devices. They show high efficiencies but these are obtained in laboratory level. However, the best PV devices used commercially are found to have efficiency around 22%. The main problem being the cost, so as the production increases cost will surely be reduced.

1.2. Solar cell generations

The photovoltaic generation is classified into three generations namely first, second and third generation based on the key materials used and its level of commercial maturity of this photovoltaic technology [19].

1.2.1 First generation Solar Cells

The first generation solar cells include single crystal solar cells and multi crystal solar cells. They are the oldest and most common used technologies due to their high efficiencies. The name crystalline Si came from the way they were made. The mono crystalline or single crystalline Si solar cells were obtained from thin wafers. These thin wafers were cut out from a single continuous crystal and the mono crystalline have usually a dark bluish or blackish colour. The monocrystalline Si has usually a pseudo shape and infinite grain boundary and mostly obtained by Czochralski and float zone process. Figure 1.2 represents a monocrystalline cell module.



Fig 1.2 Monocrystalline Si solar cells

Polycrystalline Si solar cells are made by melting the Si material and then pouring into a mold. They have a bluish color and is not as dark as mono crystalline having a grain boundary size in mm. They are much cheaper than mono crystalline and cell efficiencies are less than mono. Figure 1.3 represents a polycrystalline solar cell.

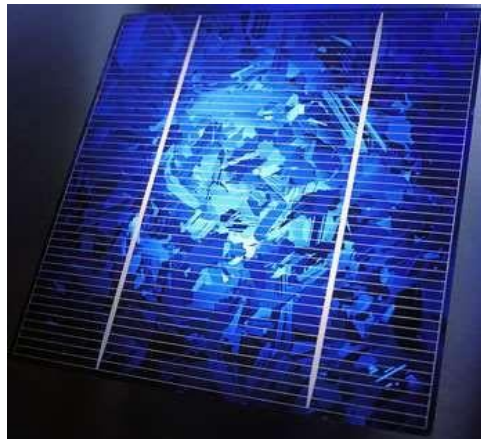


Fig 1.3 Polycrystalline Si solar cell

1.2.2. Second Generation Solar cells

The second generation solar cells involve amorphous Si (a-Si), cadmium telluride (CdTe), copper indium gallium diselenide (CIGS) alloy, etc. These solar cells are thinner, flexible to some extent and less expensive in comparison with the first generation solar cells. The amorphous Si is somewhat dark brown to purple in colour. Their efficiencies are less than the first generation solar cells. In addition, visual aesthetic is an advantage of the second generation. They are most commonly used in windows, cars etc. as these type of cells don't have any front fingers for metallization on the thin film solar cells. Figure 1.4 shows modules of amorphous Si solar cell, flexible CdTe cell and CIGS cell respectively.



Fig 1.4 (a) Amorphous Si solar cells, (b) flexible CdTe cells, (c) flexible CIGS cells

1.2.3. Third Generation Solar Cells

The third generation includes Dye sensitized solar cells (DSSC), organic polymer solar cells and nanocrystal solar cells. These are considered as novel technologies which are promising but not yet commercially proven. Their efficiency is very low but is very cost effective compared to other generations. The production of these technologies is also very easy compared to other technologies. The DSSCs can have variable color. Figure 1.5 shows a third generation solar cell.

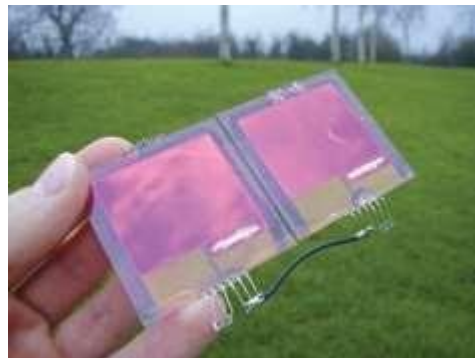


Fig 1.5 Organic solar Cells

Efficiency- 1st generation solar cells report a 26.33% lab based efficiency whereas modules report 22.7%. The 2nd generation reports 18.4% in cells and 13.4% in modules as tested in the laboratories whereas the 3rd generation solar cells reported a very high efficiency 24.2% [20, 21].

1.3 Solar Cells

A solar cell is an electronic device which directly converts sunlight into electricity based on photovoltaic effect. The important steps involved in the operation of a solar cell include:

1. Generation of light generated carriers.
2. Separation of electron-hole pair and transportation to the electrode

3. Collection of the light generated carriers to generate a current
4. Generation of a large voltage across the solar cell
5. Dissipation of power in the load.

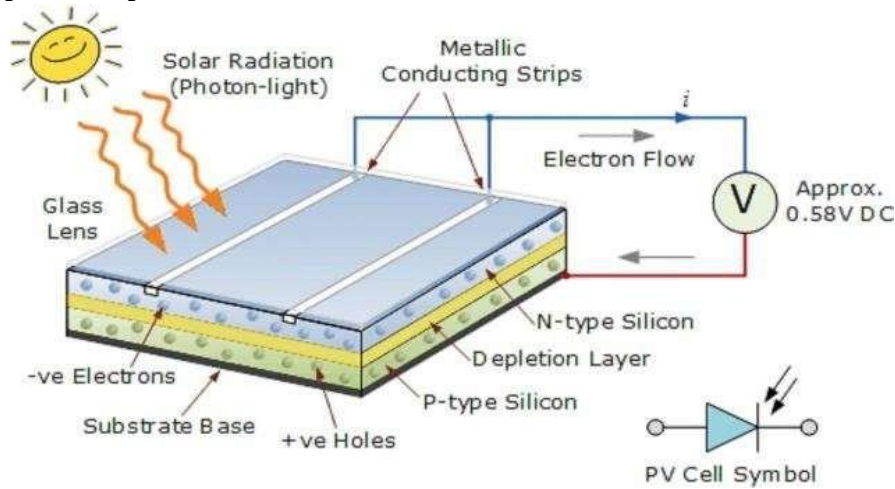


Fig 1.6 The construction of a solar cell

The most common solar cells are essentially very large area p-n junction diodes, where such a diode is formed by making a junction between n-type and p-type regions.

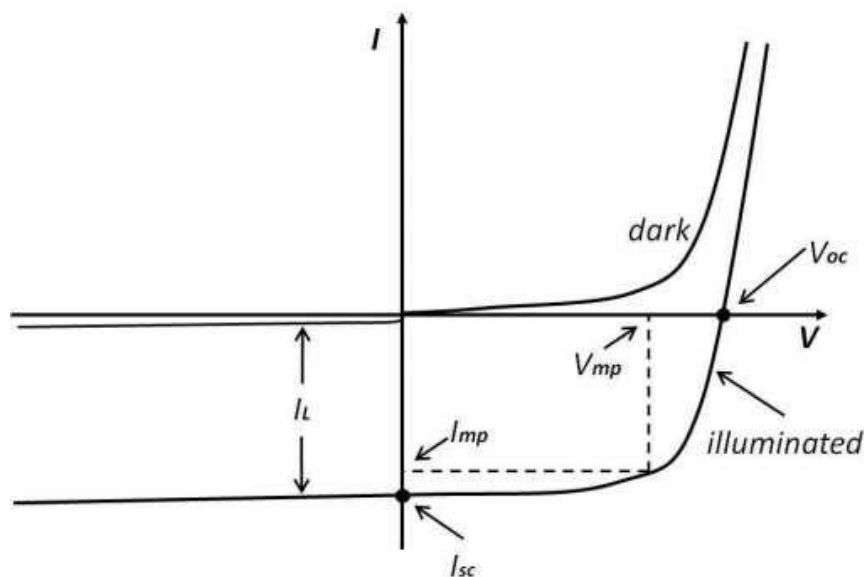


Fig 1.7 Typical I-V curve of solar cells under illuminated and dark conditions [22]

The quality or performance solar cell is evaluated by using its dark and illuminated I-V (or J-V) characteristics. The typical J-V characteristics of both light and dark conditions along with some cell performance parameters are shown in following Figure 1.7

1.4. Solar Cell Basic Parameters

Expression for net current(I) flowing across the load:

$$I = I_L - I_0 \{ \exp (q(V + I r_s)/nkT) - 1 \} - (V + I r_s)/r_{sh} \quad (1.1)$$

I_L = light generated current,

I_0 = dark saturation current,

r_s = series resistance

r_{sh} = shunt resistance

1.4.1 Open Circuit Voltage

Open circuit voltage V_{oc} is the maximum voltage that can be obtained from a solar cell when its terminals are left open. It defines the operating regime of a solar cell. A solar cell delivers power only in the region from 0 to V_{oc} . It is represented by the following equation

$$V_{OC} = (KT/q) \ln \{ (I_L/I_0) + 1 \} \quad (1.2)$$

Where, k is Boltzman's constant, T is temperature in Kelvin, q is the electronic charge.

The V_{oc} is decided by the band gap energy of the material. The V_{oc} of the solar cell will be higher if the band gap of the material is higher. As V_{oc} of Si is 1.1V, so maximum possible V_{oc} is 1.1V. However, I_0 will be lower if V_{oc} is higher.

1.4.2. Short Circuit Current

Short circuit current can be defined as the maximum current that is produced by a solar cell when its terminals are shorted. The maximum short circuit current depends on the number of photons which are a part of the solar spectrum and the potential of these photons to excite an electron. If assumed that there is no recombination in a solar cell we can obtain maximum short circuit current. It is an extensive variable as it depends on the area of the solar cell also. For Si having a band gap of 1.1V upper limit to short circuit current is almost about 46 mA/cm²

1.4.3 Fill Factor

The fill factor (FF) represents the squareness of the I-V curve. It is mainly related to the resistive losses that take place in a solar cell. Fill factor can also be defined as the ratio of the maximum output power (V_m , I_m) to the product of V_{oc} and I_{sc} . It can be related as:

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (1.3)$$

Ideally, FF can be 100% corresponding to the square I-V curve. But as there are always some or the other losses in a solar cell it's not feasible to have ideal curve. The best values of FF can be obtained from function of V_{oc} .

$$FF = \frac{voc - \ln(voc + 0.72)}{voc + 1} \quad (1.4)$$

Where voc represents thermal voltage and is given by $V_{oc}/(kT/q)$. Thus with an increase in V_{oc} the FF is higher. FF can be nearly about 0.80 for a good solar cells.

1.4.4. Power conversion Efficiency(η)

It can be defined as the ratio of the power output to the power input. The maximum power point P_m is considered as the power output of a solar cell. Power input is referred to as the incident solar radiation. The efficiency shows that how good a solar cell can convert light energy into electrical current.

$$\eta = \frac{V_m I_m}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad (1.5)$$

The efficiency of a solar cell depends on the temperature condition as well as the intensity of the solar radiation.

1.4.5. Maximum power point (P_m , V_m , I_m)

Maximum power point is the point on the illuminated I-V curve of the solar cell. At this point the solar cell produces maximum power or the product of voltage and current is maximum.

1.4.6. Parasitic Resistance

The parasitic resistance mainly includes the series and the shunt resistance. The key impact of this parasitic resistance is that it reduces the FF. These resistive effects in solar cells reduce

the efficiency of the solar cell by dissipating power in the resistances.

- **Series Resistance:** This includes the sum of all the resistances that come in the path of the current. They include the base emitter, all contacts resistance between metal and Si, resistance between top and rear metal contacts. The value of the series resistance should be as low as possible.
- **Shunt Resistance:** It is related with manufacturing defects. It is mostly due to the leakage in the P - N junction. It is desirable to have shunt resistance as high as possible. Low shunt resistance causes a huge amount of loss of power in solar cells as they provide an alternative current path for the I_L .

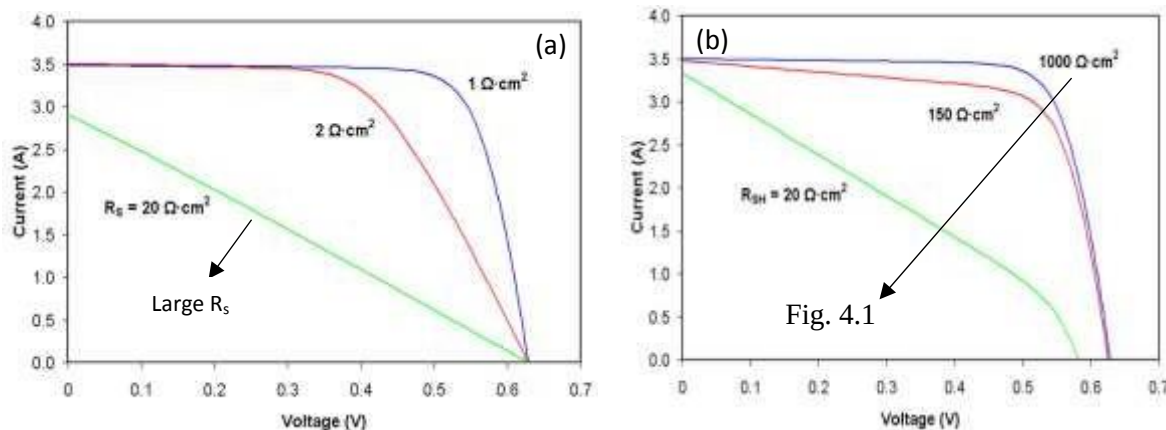


Fig 1.8 Effect of parasitic resistances on the output characteristics of solar cells (a) effect of series resistance, R_s , (b) Effect of shunt resistance, R_{sh}

1.4.7. Standard Test Condition (STC)

These are the conditions under which solar cells are tested. By using a fixed set of conditions under which solar cells can be more accurately compared and rated against each other. There are three standard test conditions. The temperature of the solar cell should be around 25°C . The solar irradiance on a clear sunny day is about 1000 W/m^2 that is received on a tilted plane surface with an angle of incidence of 48.2° . The air mass should be AM1.5G.

1.5 Model of a solar cell

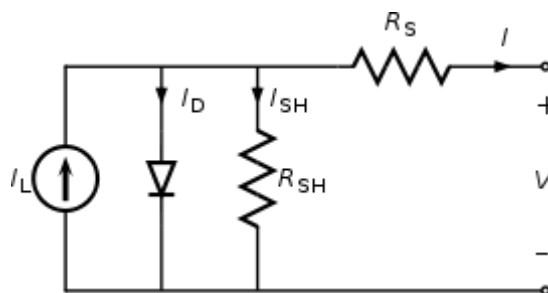


Fig 1.09 Equivalent Circuit of a p-n junction solar cell

In order to understand the electronic behavior of a solar cell, an electrically equivalent model need to be created and this based on the ideal electrical components whose behavior is well defined. An ideal solar cell can be considered as a current source where the current that is produced by the solar cell is proportional to the light intensity that is falling on the solar cell. As in practical life nothing can be ideal neither the solar cell, so the current source is kept in parallel with a diode and shunt as well as series components are also added in the model [22]. The current source itself represents the optical losses whereas the recombination losses are represented by the diode kept in parallel to the current source. In a two diode model, two diodes, both kept parallel with the current source. One diode represents the recombination losses in the bulk and the in emitter region of the solar cell whereas other diode represents the recombination losses that occurs in the space charge region of a solar cell. In a simple model the recombination that takes place in space charge region is neglected. The ohmic losses that occurs in a solar cell is represented by the shunt and series resistances denoted by R_{sh} and R_s respectively.

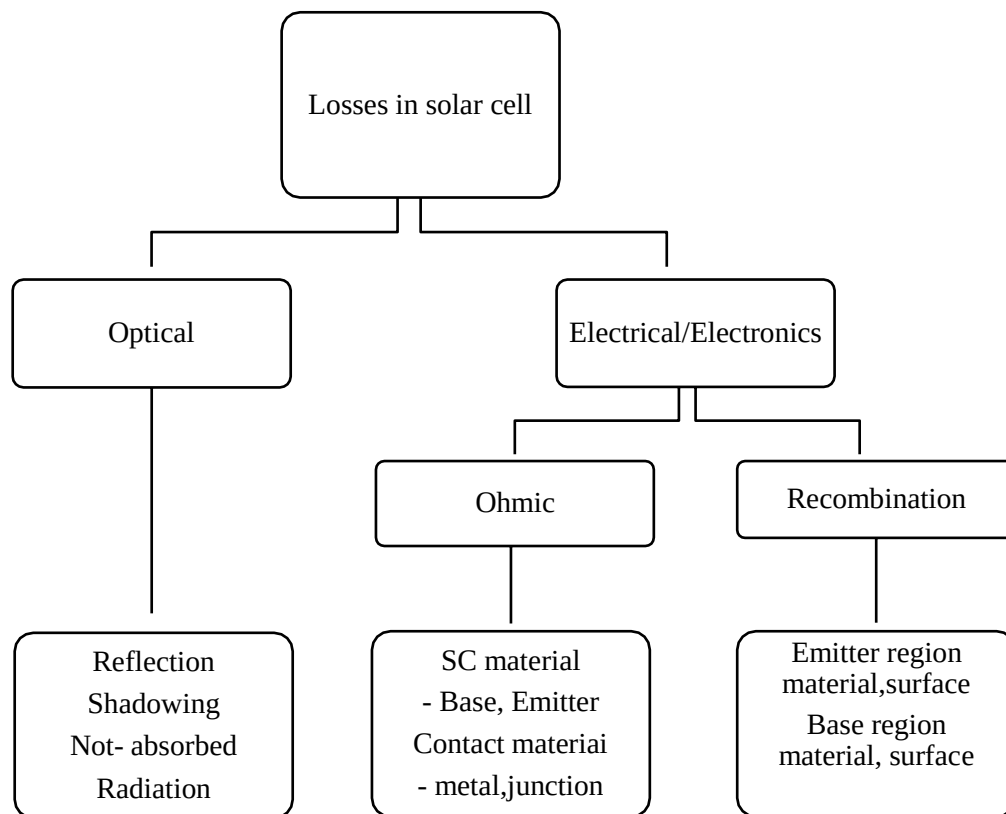


Fig 1.10 Summary of losses in solar cells

1.6. Losses in a solar cell

There are two types of losses that take place in a solar cell. They are fundamental losses and technological losses. The fundamental losses include loss of low energy photon, loss due to excess energy of photons, some voltage loss due to unavoidable intrinsic Auger recombination, Fill Factor becomes 0.89 instead of 1 (in ideal case) due to parasitic losses. These fundamental losses are unavoidable. The losses shown in Fig 1.10 could be avoided to some extent by adopting special fabrication techniques.

Thus the basic challenges or the limiting factors for high efficiency Si are:

- Relative high optical loss, shadowing, etc.,
- High recombination losses mostly at the rear surface
- High contact resistance causing resistive losses

The options for improvement of this technological losses in order to improve the efficiency of the solar cells are as follows:

- ❖ **Minimize recombination**- As not all the generated electron hole pairs can contribute to solar current and voltage and this is mainly due to recombination. Proper surface and bulk passivation is needed in order to reduce it. Improvement of the material quality like using n-type Si and by means of heavy doping by local doping, selective emitters can be done. Besides these use of effective surface passivation layers such as SiN_x , SiO_2 , Al_2O_3 , etc. and low recombination contacts such as heterojunctions are also helpful for minimizing recombination.
- ❖ **Minimize optical losses**- a part of the incident photon is always reflected from cell surface and this can be reduced by using anti reflective coatings, surface texturing and plasmonic structures. In order to reduce losses due to incomplete absorption proper light trapping schemes need to be adapted. The shadow losses due to metal coverage can be reduced by using rear contact designs, transparent contacts, etc.
- ❖ **Minimize resistive losses**- In order to increase the conductance and reduction of losses due to resistance advanced electrode architecture, materials and proper rear contact designs need to be used.

1.7 Minimization of Optical loss by SiNW array

In order to reduce these losses and promote high efficiency solar cell technology, several advanced cell structures have been developed and progressed over years. To increase the efficiency in planar c-Si solar cells it involves-1] large amount of material to absorb good amount of solar light which requires anti reflection coating that enhances the cost.2] There is also a need of long minority carrier diffusion length and for this it needs a very high quality material.

All these problems can be overcome by using SiNW arrays. SiNW has a unique 3-D structure which helps in excellent light trapping capability as well reduces the cost. These also exhibit higher absorbance per unit thickness. Nowadays, NW arrays are becoming more attractive due to its unique electrical and optical properties as compared to bulk Si[23-25]. There are several methods that are reported for the synthesis of these SiNW arrays. P-N junction with radial NW array increases the light absorption capability if the length of these SiNW arrays can be increased. Beside this, it can also offer a short carrier collection path in the radial direction in contrast to planar Si. Garnet and Yang reported that the path length of incident solar radiation (AM1.5G spectrum) in SiNW array films increases by 73 times[26]. These advantages of the SiNW arrays dilute the need of high quality Si material having long minority carrier diffusion length and also need of an extra anti reflective coating. In spite of all these advantages, there were many problems that need to be solved while fabricating SiNW based solar cell related to the power conversion efficiency (PCE). However, the higher cost for the synthesis of SiNW array on wafer scale was the biggest disadvantage. Earlier NW synthesis techniques (both bottom up and top down methods) were time consuming as well as costly techniques. With the advent of the simple and low cost metal catalyzed electroless etching (MCEE) technique the issues of SiNW array production came to an end. But still there is a challenge in fabrication of radial junction using SiNW produced by MCEE technique as the average diameter of the NW is about 125nm [27, 28]. So during fabrication of radial junction by familiar semiconductor device processing technologies (like thermal diffusion, core-shell structure by VLS method) depleted the NWs and even for small diameter NWs polarity changes completely. With the core-shell structure prepared by VLS technique problem of low crystalline quality for shell layers plays a major role. So advantages of radial junction as predicted by theory cannot be exploited with these thin SiNW. In addition to these problems, increased surface recombination due to the huge surface area of such NW geometry reduces the device performance substantially. In place of SiNW if Si microwires (SiMWs) with diameter in the range 1 to 2 micron could be used then it is possible to fabricate radial p-n junction inside the same micro wire by thermal diffusion process.

Advantages of nanowire Geometry

- SiNW arrays have excellent antireflection and light trapping properties.
- It helps to increase the path length of incident solar radiation on SiNW array films by 73 times for AM1.5G illumination [26].
- It shows low reflectance of less than 10% with a strong broadband optical absorption. The low reflectance of SiNW array offers advantage of incident light trapping within the NW arrays.

- In the NW arrays, there is collective light scattering interaction which allows light to travel much longer distance by many turns than the NW length and the ultrahigh surface areas of high-density SiNW increase the absorption.
- The antireflection as well as light trapping property of SiNW arrays depend on NW lengths, diameters, alignment and spacing. As the NW length increases, reflection also decreases.
- The nanowires help in minimizing the losses at each step which in turn cut down the solar production cost.
- In Si core shell NWs, there is over 100% enhancement of photocurrent as compared to only NWs without shell [29].
- In radial p-n junction core shell structures, excellent carrier separation and propagation take place via the built in electric fields of radial p-n junctions [30, 31].

Advantages of microwire arrays

- SiMW allows successful formation of radial junction within same MW.
- They are mostly used due to their low cost, high efficiency and photochemical generation [32-34].
- These high aspect ratio, radial junction wire arrays allow the absorption of nearly all the incident sunlight in visible region while enabling efficient carrier extraction in the radial direction [35], even in low-quality materials with relatively short minority carrier diffusion lengths [36].
- These wire arrays can be embedded in a polymer and removed from the substrate yielding lightweight, flexible solar cells, while preserving the relatively expensive growth substrate for reuse [37].

References

1. F. Morton, Proceedings of the National Academy of Sciences, **104**, 19680-19685 (2007).
2. C. Parmesan and G. Yohe, Nature **421**, 37-42 (2003).
3. M. Edwards and A. J. Richardson, Nature **430**, 881-884 (2004).
4. (a) C. Rosenzweig and M.L. Pery, Nature **367**, 133-138 (1994). (b) M. S. Dresselhaus and I. L. Thomas, Nature **414**, 332 (2001).
5. J. Potocnik, Science **315**, 810 (2007).
6. N. S. Lewis, Science **315**, 798 (2007).
7. M. I. Hoffert, K. Caldeira, G. Benford, D. R. Criswell, C. Green, H. Herzog, A. K. Jain,

- H. S. Khesghi, K. S. Lackner, J. S. Lewis, H. D. Lightfoot, W. Manheimer, J. C. Mankins, M. E. Mauel, L. J. Perkins, M. E. Schlesinger, T. Volk and T. M. L. Wigley, *Science* **298**, 981 (2002).
8. A. Fujishima and K. Honda, *Nature* **238**, 37 (1972).
9. Quantifying Energy: BP Statistical Review of World Energy, June 2006, <http://tinyurl.com/22s49l>
10. J. Chow, R. J. Kopp and P. R. Portney, *Science* **302**, 1528 (2003).
11. G. M. Whitesides and G. W. Crabtree, *Science* **315**, 796 (2007).
12. 2014 Key World Energy Statistics (IEA, 2014, p 6). <http://www.iea.org/publications/freepublications/publication/keyworld2014.pdf>.
13. Renewables 2014 Global Status Report (REN21, 2014, p. 21). http://www.Ren21.net/Portals/0/documents/Resources/GSR/2014/GSR2014_KeyFindings_low%20res.pdf.
14. J. Nelson, *The physics of solar cells*. 2003: World Scientific Publishing Co Inc.
15. A. Goetzberger, and C. Hebling, *Photovoltaic materials, past, present, future*. Solar Energy materials and solar cells, **62**, 1-19 (2000).
16. W. Zulehner, *Czochralski growth of Si*. Journal of Crystal Growth, **65**, 189-213 (1983).
17. S. -S. Sun, and N. S. Sariciftci, *Organic photovoltaics: mechanisms, materials, and devices*. 2005, CRC press
18. L. Kazmerski, D. Gwinner and A. Hicks, *Best research cell efficiencies*. National Renewable Energy Laboratory **2**, 0.0-2.0 (2010).
19. K. Ranabhat et al., *Journal of Applied Engineering Science* **405**, 481-491, 14 (2016)4.
20. M. A. Green et al, “Solar cell efficiency tables (version 50)”, *Progress in Photovoltaics* **25**, 668, (2017).
21. <http://org.ntnu.no/solarcells/pages/history.php>
22. P. Sidi, P. Nji, R. Poespawati and D. Hartanto, *Solar Cells – Si Wafer Based Technologies* (2011) 10.5772/19935
23. S. F. Duan, Y. Huang, R. Agarwal and C.M. Lieber, *Nature* **421**, 241–245 (2003).
24. Y. Juang, X. F. Duan and C. M. Lieber, *Small* **1**, 142–147 (2005).
25. K. Q. Peng, Y. J. Yan, S. P. Gao and J. Zhu, *Adv. Matter* **14**, 1164–1167 (2002).
26. S. Xu, S.Y. Huang, I. Levchenko, H. P. Zhou, D. Y. Wei, S. Q. Xiao, L. X. Xu, W. S. Yan, and K. Ostrikov, *Adv. Energy Mater.* **1**, 373 (2011)
27. H. P. Yoon, Y. A. Yuwen, C. E. Kendrick, G. D. Barber, N. J. Podraza, J. M. Redwing

- T.E. Mallouk, C.R. Wronski, T.S. Mayer, Appl. Phys. Lett. **96**, 213503 (2010)
28. O. Gunawan, S. Guha, Sol. Energy Mater. Sol. Cells **93**, 1388 (2009)
 29. M.D. Kelzenberg, S.W. Boettcher, J.A. Petykiewicz, D.B. Turner-Evans, M.C. Putnam, E.L. Warren, J.M. Spurgeon, R.M. Briggs, N.S. Lewis, H.A. Atwater, Nat. Mater. **9**, 239 (2010).
 30. K. Sato, M. Dutta, N. Fukata, Nanoscale **6**, 6092 (2014)
 31. M. Dutta, N. Fukata, J. Nanosci. Nanotechnol. **15**, 4339 (2015)
 32. S. W. Boettcher, E. L. Warren, M. C. Putnam, E. A. Santori, D. B. TurnerEvans, M. D. Kelzenberg, M. G. Walter, J. R. McKone, B. S. Brunschwig, H. A. Atwater, and N. S. Lewis, J. Am. Chem. Soc., **133**, 1216– 1219 (2011).
 33. E. L. Warren, S. W. Boettcher, M. G. Walter, H. A. Atwater, and N. S. Lewis, J. Phys. Chem. C, **115**, 594–598 (2011).
 34. A. P. Goodey, S. M. Eichfeld, K.-K. Lew, J. M. Redwing, and T. E. Mallouk, J. Amer. Chem. Soc., **129**, 12344– 12345,(2007)
 35. M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis, and H. A. Atwater, Nat. Mater., **9**, 239–244, (2010).
 36. B. M. Kayes, H. A. Atwater, and N. S. Lewis, J. Appl. Phys., **97**, 114302-1–114302-11 (2005).
 37. J. M. Spurgeon, K. E. Plass, B. M. Kayes, B. S. Brunschwig, H. A. Atwater, and N. S. Lewis, Appl. Phys. Lett., **93**, 032112, (2008).

Chapter2

Characterization techniques

The characterization techniques involve morphological, electrical as well as optical studies.

2.1 Morphological Characterization

2.1.1 Scanning Electron Microscopy

The scanning electron microscope most popularly known as SEM is used to study the morphology or the surface, topographical features, phase distribution, difference in the composition, also if there is presence of any electrical defects within the specimen. It uses focused beam of electron to generate highly magnified view of the substrate. In SEM, when the specimen is irradiated with a fine electron beam which is also called an electron probe, secondary electrons are emitted from the specimen surface. Then the topography as well as the morphology of the surface of the specimen can be observed by a two dimensional scanning of the electron probe over the surface and the acquisition of an image from the detected secondary electrons.

The construction of the SEM is that it consists of an electron optical system which produces an electron probe, a specimen stage that is used to hold the specimen, a secondary- electron detector to collect the secondary electrons, an image display unit and also an operation unit to perform the various operations.

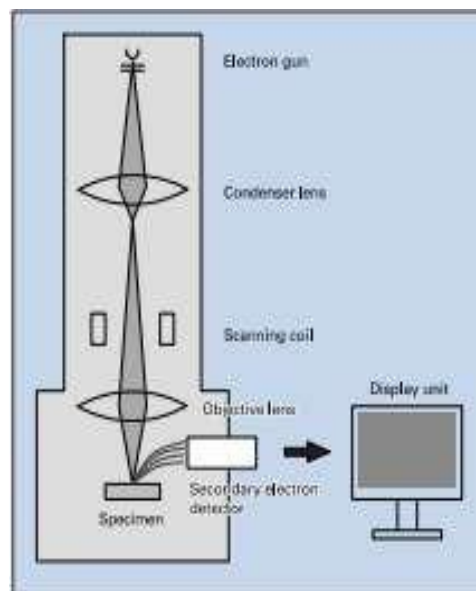


Fig. 2.1 Basic Construction of SEM

The electron optical system consists of electron gun, a condenser lens and an objective lens to produce an electron probe, a scanning coil and all other components. The electron optical system and the entire space surrounding the specimen are all kept at vacuum.

The electron gun also called Thermionic emission (TE) gun is used to produce an electron beam. Thermoelectrons are emitted by heating the filaments referred to as cathode made of thin tungsten wire at high temperature usually 2800K. These emitted thermoelectrons are gathered as electron beams which then flow into the metal plate called anode when a positive voltage is applied to the anode. Besides the TE gun other guns also include field emission electron gun (FE) gun or Schottky emission electron gun (SE) gun. After that a lens is placed below the electron gun which helps to adjust the diameter of the electron beam. The electron beam from the electron gun is focused by the two stage lenses which include condenser lens and the objective lens, and together a small electron probe is produced. The main function of the condenser lens is that the adjustment of the excitation of the condenser lens helps to change the electron probe diameter as well as the probe current.

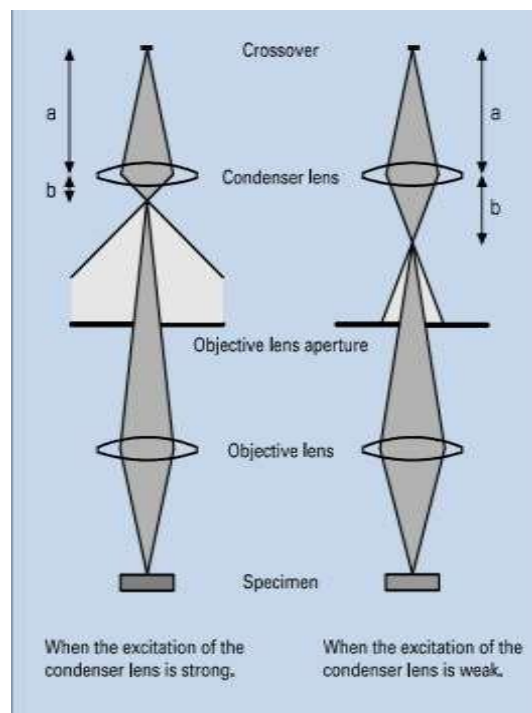


Fig. 2.2 Formation of electron probe by lenses.

The objective lens used for mostly focusing and also plays an important role in determining the final diameter of the electron probe.

The specimen stage is used as it stably supports the specimen and provides smooth movement when required. The specimen stage provides horizontal movement (X, Y), vertical movement (Z), specimen tilting (T) and also rotation (R). X and Y movement help to select the field of view, z help to change image resolution and depth of focus.

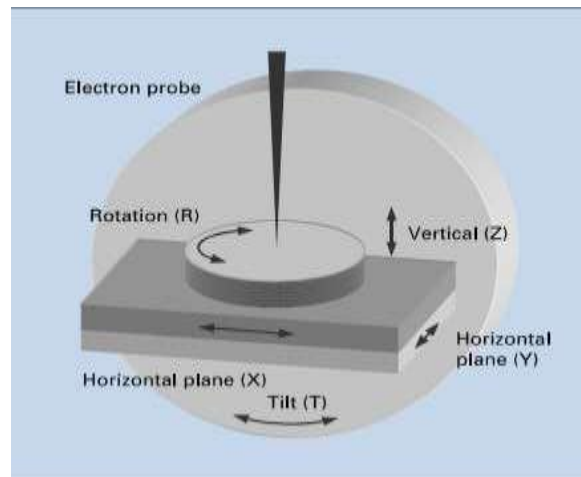


Fig.2.3 Construction of Specimen Stage

Now comes the secondary electron detector which detects the secondary electrons that are emitted from the surface of the specimen. There is a scintillator or a fluorescent substance coated on the tip of the detector and a high voltage of about 10KV is applied. The emitted secondary electrons are then attracted towards the high voltage and generate light on hitting the scintillator. The light-guide directs the light to a photo multiplier tube (PMT). Light then converted to electrons which then amplified as an electric signal.

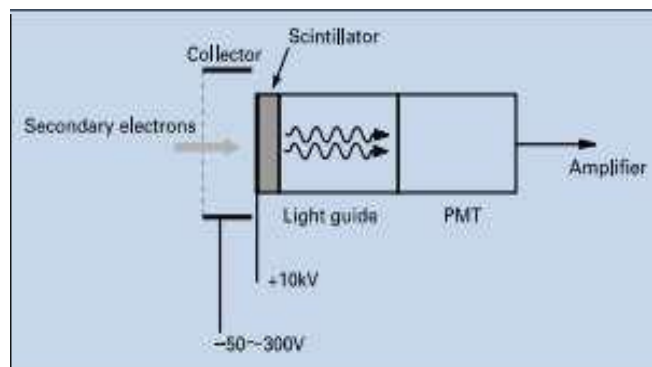


Fig. 2.4 Construction of Secondary Electron Detector

The output signals that comes out of the secondary electron detector are then amplified and transferred into a display unit or LCD (liquid crystal display). Additional field-emission cathode in the electron gun of a scanning electron microscope (which is called FESEM) provides further narrower probing beams at low as well as high electron energy, resulting in improved spatial

resolution with the highest magnification possible and also reduces the possibility of charging the sample and damage for the application to a minimum. Sometimes an arrangement is attached to the instrument for energy dispersive X-ray analysis (EDS). EDS identifies the elemental composition of the material imaged in the SEM for all elements with atomic number greater than boron. This depends on the generation of the x-ray fluorescence from the atoms which are struck by the scanning beam. The x-ray photon is a characteristic of the element from which it is produced. These photons are collected and analyzed to get the signature of its mother element.



Fig..2.5 Scanning Electron Microscope (SEM) system.

2.2 Optical Characterization

2.2.1. UV-Vis Spectrophotometer

The ultraviolet and visible (UV-Vis) absorption spectroscopy is mostly used for the measurement of the attenuation as well as the reflection of the beam light after it passes through the sample surface. This device includes a variety of absorption, transmittance, and reflectance measurements in the ultraviolet (UV), visible and near-infrared (NIR) spectral regions.

The spectrophotometer mostly consists of deuterium discharge lamp for UV measurements and a tungsten halogen filament lamp for visible and NIR measurements. This spectrophotometer has the ability to automatically swap lamps when it will be scanning UV and visible regions. These light sources are directed into a single or double monochromator. The monochromator is a combination of entrance slit, lens gratings or prism and an exit slit. The radiation source enters through the entrance slit which is then focused by the

collimating lens on the gratings. These gratings are an advancement of the prism and the surface of gratings consist of many small prisms. The focused light is dispersed by this holographic grating into seven parts called VIBGYOR in the monochromator or commonly called spectrograph. Then the selected optimum radiation comes out of the exit slit. This dual beam design is mostly used for measuring the light power after (P) and light power before (P_0) of the samples as well as reference. Then the radiation strikes the chopper where it is converted into two parts. Now-a-days most spectrometer uses a rotating chopper wheel to alternately direct the light beam through the sample and reference cell. One part of the radiation strikes the sample and the other part strikes the reference. There are two detectors present at the sample and the reference cell to detect the radiation and convert it into electric signals.

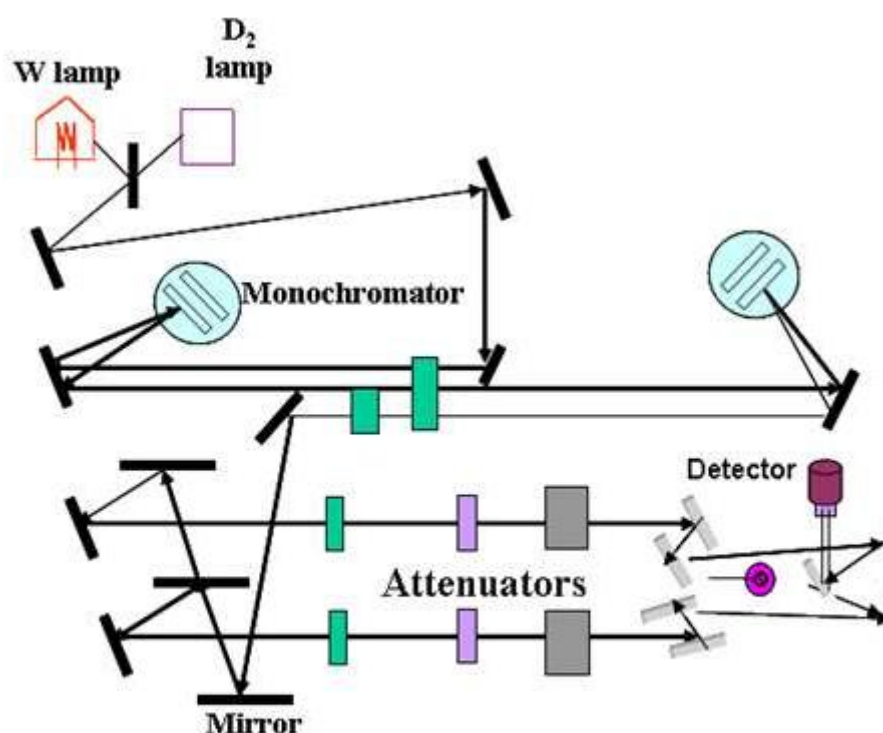


Fig. 2.6 Schematic diagram of a UV-Vis spectrophotometer

There are three types of detectors used in the UV-Vis spectrophotometer. They are:

- Photo multiplier tube (PMT) detector: In this the photons striking the PMT detector gets converted into electrons and are also multiplied.
- Photodiode array (PDA) detector: Diodes are also present which converts electromagnetic radiation or UV-Vis radiation into electrical signals.

- Charged coupled Detector (CCD): In this there is a silicon surface and when radiation in the form of photon strikes this silicon surface and will be converted into digital signals by using CCD.

The detected electronics or software program can then manipulate the P and P₀ values as the wavelength scans to produce the spectrum of absorbance or transmittance as function of wavelength.

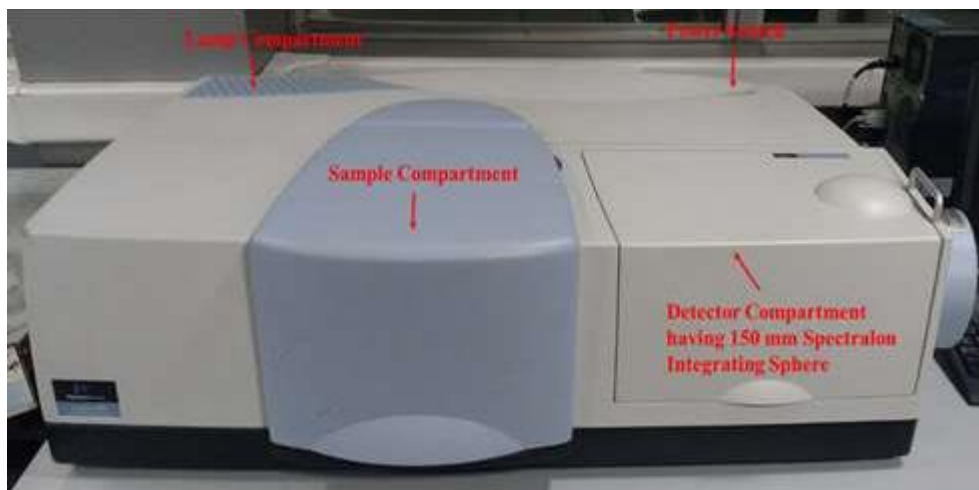


Fig. 2.7 UV- Vis Nir Spectrophotometer- LAMBDA 1050 with dual compartments and 150 mm snap-in integrating sphere

PerkinElmer LAMBDA 1050 is used as it has unique polarization measurement capabilities to match our analytical needs.

1. Deuterium and Tungsten halogen Light sources with doubling mirror for ultra high sensitivity.
2. Double Holographic Grating Monochromator which provides ultra-low stray light performance.
3. Common Beam Mask allows precise adjustment of beam height to match samples of different dimensions.
4. Common Beam Depolarizer corrects for inherent instrument polarization to allow accurate measurements of birefringent samples. However this is optional.
5. Chopper switches between the samples and reference beam
6. Sample and reference beam attenuator is used for extreme sensitive and accurate measurements on highly absorbing samples.
7. Sample compartment
8. Photomultiplier and Peltier controlled PbS Detectors provides full range UV/Vis/NIR coverage from 200 to 3300nm.

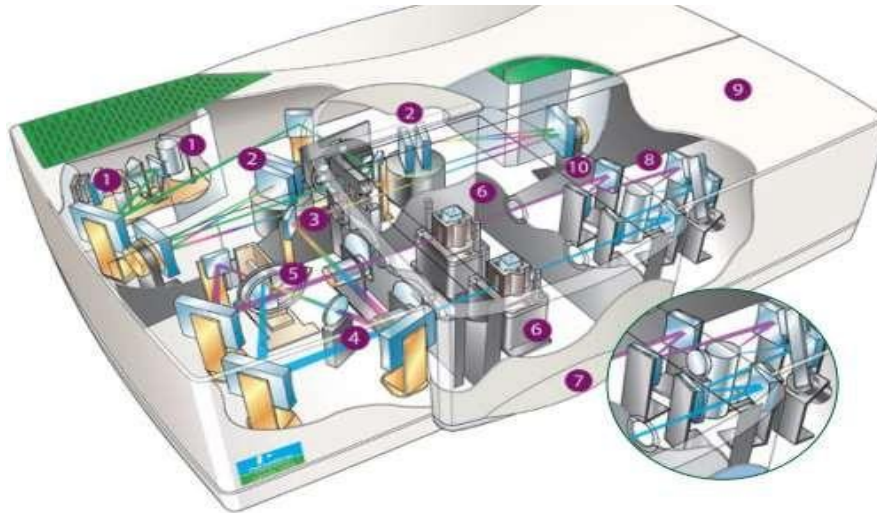


Fig.. 2.8 Inside View of LAMBDA

9. Second sampling Area houses a range of snap-in sampling modules including transmission optics
150 mm integrating spheres and universal reflectance accessory
10. Photomultiplier and Peltier controlled PbS Detectors

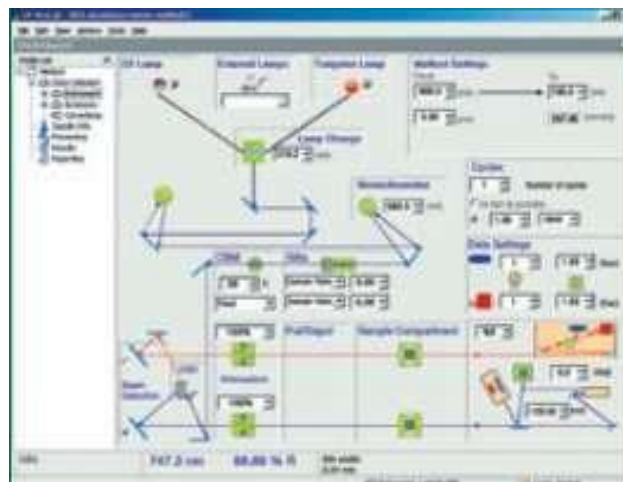


Fig.. 2.9 UV WINLAB software

The UV WINLAB software guides the user from setup to results. It helps in the method development reporting and the analysis of the results obtained in simple steps.

2.3 Electrical characterization

2.3.1 Quantum Efficiency and Current density (J) - Volatge (V) Measurement System

Quantum efficiency (QE) is an important measurement tool to investigate the performance of the solar cell. This is helpful for designing high efficiency solar cells. QE helps to measure the short circuit current density

(J_{sc}) of the device at each wavelength of the solar spectrum. The standard test conditions being 100 mW/cm^2 AM 1.5 G at 25°C . It provides information about recombination process active in the material and also about the quality of the passivation layer. The QE measurement provides qualitative information whereas the J-V characteristic provides estimation of the maximum power that can be extracted from the solar cells. Thus has lot of significance in research and development of the solar cells. The quantum efficiency can be integrated to obtain short circuit current density which can be matched with that obtained from J-V measurement in a good solar cell device.



Fig. 2.10.: M/s Bunkoukeiki (Model: CEP-25HS50)

There are two types of QE. They are external QE (EQE) and internal QE (IQE). EQE is defined as the ratio of the number of electrons that are collected by the solar cells to the number of photons of a given energy incident from outside. IQE is defined as the ratio of number of the electrons that are collected by the solar cell to the number of photons of a given energy absorbed by the solar cell.

$$EQE = \frac{\Delta J_{sc}}{q \Delta \phi \lambda} \quad 2.1$$

$$IQE = \frac{EQE}{1 - R(\lambda) - T(\lambda)} \quad 2.2$$

The two equations shown above represent EQE and IQE respectively. The ΔJ_{sc} represents the increment in short circuit current generated by the solar cells for incident incremental photon flux of $\Delta \phi_\lambda$ at a wavelength

of λ . The main difference between EQE and IQE is that EQE does not include the transmission and the reflection losses while the IQE include both the optical losses.

In order to measure QE and J-V characteristics of samples M/s Bunkoukeiki (Model: CEP-25HS 50) is used which can hold samples having maximum size of 5cm x5cm and this is limited by the size of illumination source uniformity. In this set-up light source is Xenon lamp and the light is guided to the sample stage through set of optical assembly.

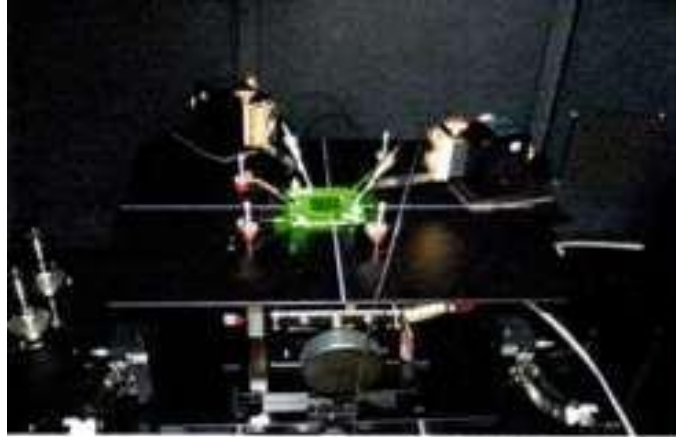


Fig. 2.11: Solar cell sample stage

For the J-V measurement, an AM 1.5G filter is used for white source ($100\text{mW}/\text{cm}^2$). On the other hand in order to measure the QE, there are grating monochromator based optical filters and a set of optical assembly, lock in amplifier, etc. and the wavelength can be varied by steps of 1 nm to 50 nm. In this spectral response (SR) measurement, the photocurrent density from the solar cell is measured with respect to monochromatic light of specific wavelength of fixed intensity. The SR is measured in the spectral region 300-1200 nm. EQE can be determined using the following relation,

$$SR = \frac{q\lambda QE}{hc} \quad 2.3$$

Where q is referred to as the electronic charge, λ is the wavelength of the incident light, h is the Planck's constant and c is the velocity of the light.

This J-V measurement under the standard test condition of illuminated radiation is the primary characterization test of a solar cell device. From this characterization curve obtained we can calculate all other cell parameters and also the power conversion efficiency of the device. The Xenon lamp being the source of radiation, its intensity and operation is controlled by the power supply system. As mentioned earlier the light from the xenon lamp is passed through an AM 1.5 G filter which says that the light is AM

1.5 G is of stipulated intensity. Before any measurement, the intensity of the Xenon lamp is measured using a standard photodiode which is used as a reference cell.

2.3.2 Resistivity Measurements

Resistivity of Silicon is an important parameter that has to be measured in order to get information about the electrically active impurities that are present. There are various methods measuring the bulk resistivity.

Among many methods of resistivity measurement, we will be discussing about the Four Probe Method which we have use

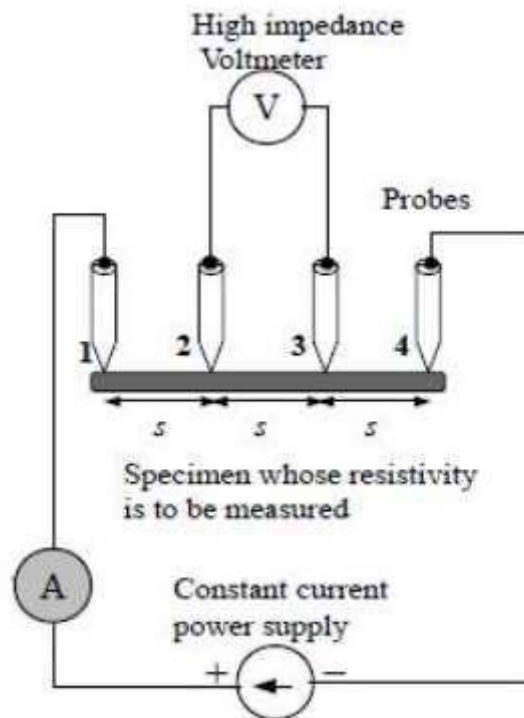


Fig. 2.12: Arrangement of four probes that measure voltage (V) and supply current (A) to the surface

Collinear Four- Point-Probe method: This method consists of four probes in a line which is placed at equidistant from each other. This method is not much accurate for measurement of polycrystalline material. The distance between two adjacent probes S is usually 1 mm. In this set-up, four spring loaded probes are pressed against the surface and current is passed through the outer probes and the voltage is measured across the two inside probes.

The contact resistance is measured by the following equation,

$$Rc = \frac{V}{I} \quad 2.4$$



Fig. 2.13: Resistivity measurement system of a solar cell (Four Probe)

This collinear four probe resistivity measurement is also used to measure the radial resistivity variation of the silicon samples as well. This can be calculated by the equation,

$$\rho = 2\pi S * \frac{V}{I} \quad 2.5$$

Where V is the potential difference between inner probes in volts.

I – Current through the outer pair of probes in ampere.

S is the Spacing between the probes in meter.

Chapter 3

Performance limitation of Si Nanowire solar cells: Effects of nanowire length, surface defects and light trapping

3.1. Introduction:

Silicon nanowires (SiNWs) have attracted global attention as a promising material to achieve high efficiency at low cost due to their unique structural, optical, and electrical properties [1, 2]. As Si has low absorption in the visible and near infrared region of the solar spectrum, so efficient commercial Si solar cells to fully absorb incident sunlight need relatively large amounts of high-purity solar-grade Si. In this decade, worldwide effort has been started to address this problem by fabricating SiNW based solar cells. Due to light-trapping within the NW arrays these cells exhibit a higher absorbance per unit thickness compare to commercial Si solar cells and thus open a path to avoid the need of extraantireflection coating layer that could lower the production cost [3].

There are several processes like CVD, molecular beam epitaxy, reactive ion etching in addition to lithography, metal catalyzed electroless etching (MCEE) technique etc. which are used to fabricate SiNWs [4]. Among these MCEE technique is only simple and low-cost while others are costly and time consuming. By MCEE technique SiNWs could be fabricated in wafer scale and the electrical characteristics of the SiNWs are same as mother Si wafer. Formation of homo or hetero junction could be achieved either by thermal diffusion or deposition of opposite polarity shell layer over the NWs in core-shell morphology by CVD technique or by spin coating opposite polarity polymer layer. Thermal diffusion involved high temperature processing while in CVD technique low temperature processing could be used. On the other hand polymer coated heterojunction cells most of the time are prepared at room temperature but subjected to reliability and stability issues. Low crystalline quality of the shell layers deposited by CVD technique most of the time degraded the performance of SiNW solar cells produced in core-shell morphology. In these SiNW solar cells surface states plays a dominant role. With increase of surface area surface related defect recombination starts to take over other types of recombination process (e.g. bulk recombination). Reduction of surface roughness helps in reducing surface recombination. This has direct effect on cell efficiency by improving efficiency from 0.5% to 5.3% [5, 6]. On the other hand insertion of thin intrinsic-Si layer improves the efficiency up to 7.29% [7]. Reduction of length of the SiNWs also showed improvement of cell efficiency up to a certain height of the NWs. In this study p-n junctions were fabricated in core-shell morphology by depositing p-Si

shell layer over n-SiNWs by cold walled thermal CVD [6]. The control of surface states of the SiNW array solar cells fabricated by thermal diffusion process has rarely been investigated. The simple way to control these surface states is to shorten the NW length that has been proved in our previous work [6]. Here we report a control over the surface states by controlling the NW height for the thermally diffused SiNW solar cells. Without using any surface or interface passivation layer this investigation shows more than 30% enhancement in cell efficiency. Thus through this work we have established a compromise between enhanced junction area and increased surface defect states with increase of NW length. This study is worth for the commercial Si solar cell production where SiNW arrays could be used as a light trapping layer instead of depositing any extra antireflection coating layers.

3.2. Experiment:

3.2.1 Procedure

SiNW arrays were prepared by MCEE technique on 300 μm thick p-type (100) single side polished crystalline p-Si substrates with resistivity of 5-10 ohm-cm. The Si substrates were cleaned with acetone (10 min) and ethanol (10 min) by sonication and then rinsed with deionized water 2–3 times and boiled in a 3:1 mixture of H_2SO_4 (96%) and H_2O_2 (30%) for 15 min and rinse by (deionised) D. I. Water thoroughly. After dipping in 2% HF for 2 minute immediately transferred to a Teflon beaker containing a solution of 0.04M of AgNO_3 in 7.8% of HF for specific time to form vertically-aligned Si NW arrays. The substrates were then rinsed thoroughly with DI water. The etched Si substrates were immersed in a solution of ammonia and hydrogen peroxide in 7:3 ratios for 10 min to remove Ag den-drites which had been deposited during etching. Again the water treatment is done 2-3 times. After this nitric acid treatment was done in order to remove Ag remnant (if any).

The P507 (phosphorous dopant solution) has been spin coated on the SiNW arrays and planar substrate. Before spinning the phosphorous containing solution on the NWs, cleaning of SiNW arrays were done by using acetone for 5 min, then by ethanol for 5 min. After this, substrates are boiled in piranha solution for 15 min at 70°C. The substrates are then washed with water for several times then dipped in 2% HF and thoroughly rinsed with de-ionized water twice. After the spin-coating the substrates were heated at 90°C for 10 min on the hot plate and at 200°C in oven for 15 min. After that we used the diffusion furnace to diffuse P on the front surface at 990°C for a chosen time period. Diffusion of dopant creates PSG layer. Now to remove PSG these Si substrates were dipped in 2% HF solution for 5 min and thoroughly washed by deionized water.

For fabrication of Al electrode on the back surface electron beam evaporator at a base pressure $\sim 3 \times 10^{-6}$ mbar was used. Thickness of the electrode was kept around 1 μm . After deposition of back contact BSF formation was achieved. Ag electrode in finger grid pattern was deposited by electron beam evaporator at a base pressure $\sim 3 \times 10^{-6}$ mbar. Contact sintering was done after that to achieve ohmic contact. The effective area of the solar cells was kept at 1 cm^2 .

3.2.2 Characterization

A Scanning Electron Microscope (SEM, Model: ZEIS EVO MA 10) was used for microstructural characterization. J-V and EQE characterizations were performed through M/s Bunkoukeiki system.

3.3 Results and Discussion:

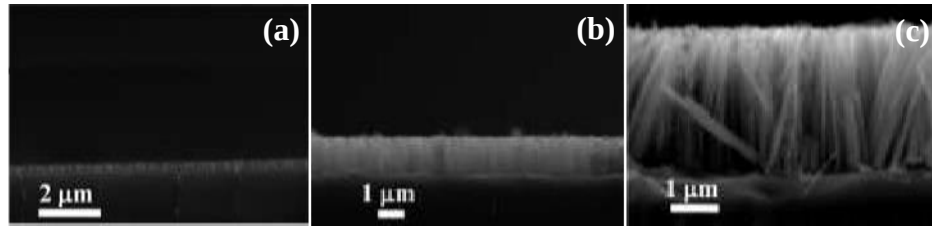


Fig. 3.1. Cross sectional SEM images of the SiNW array solar cells having SiNW length of (a) 320 nm, (b) 1550 nm, (c) 6400 nm

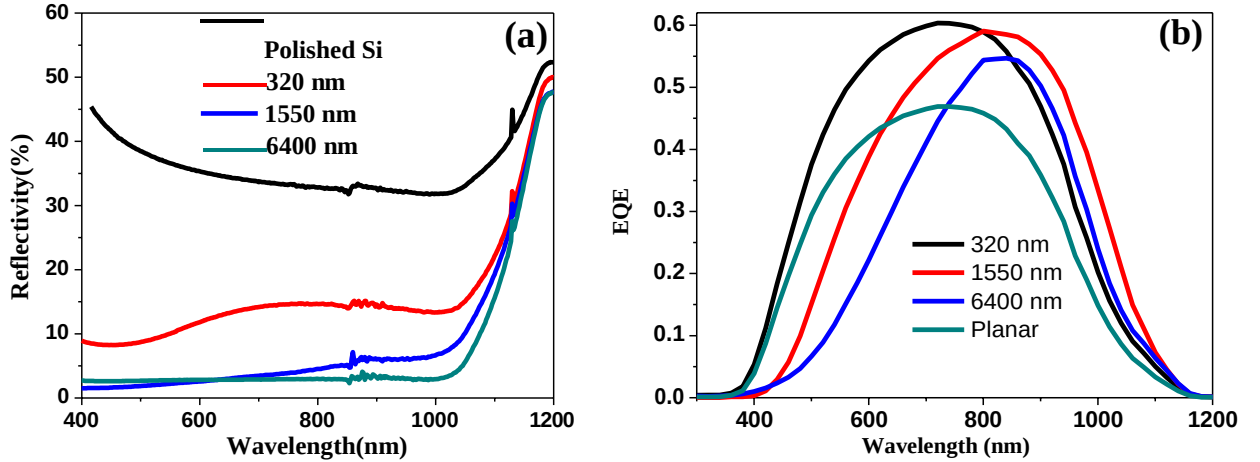


Fig. 3.2. (a) Reflectance spectra SiNW arrays of different NW length and polished Si (b) EQE of the SiNW array solar cells and planar solar cell

Fig. 3.1 shows the cross-sectional images of the SiNW arrays solar cells having different NW lengths from 320 nm to 6400 nm. Fig. 3.2 (a) shows the reflectance spectra of the SiNW arrays of different NW length and polished Si (planar) in the range of 400-1200 nm. The sharp transition occurred around 1000-1150 nm corresponds to the band edge [8]. Planar Si shows reflectance from 45-30% in the

specified range. While for SiNW arrays this reduced dramatically over a broad spectral range of 400-1000 nm. This low reflectance could be attributed to the sub-wavelength light trapping and collective light scattering within NW arrays [9, 10]. It could be also noticed from the reflectance spectra that with increase of NW length reflectance decreases more and more. External quantum efficiency (EQE) of the SiNW array based cells and planar cell are shown in Fig. 3.2 (b). A spectrally broad EQE has been observed for the planar cell. The EQE shows increment for

the all SiNW array cells compare to planar cell with some special features. It has been found that at short wavelengths EQE significantly decreased with increasing NW length. With increase of NW length roughness increases as NWs surface are rough. This increase of roughness with increase of surface area increases the surface related dangling bond defects that enunciate more surface recombination with increase of NW length [6]. From Fig. 3.2 (a) it is clear that with increase of SiNW length light trapping increases and as a result reflection reduces more and more with increase of SiNW length. However, for longer wavelengths EQE of SiNW array solar cells show some enhancement that could be ascribed to enhance light trapping. With increase of NW length at longer wavelength due to light trapping EQE

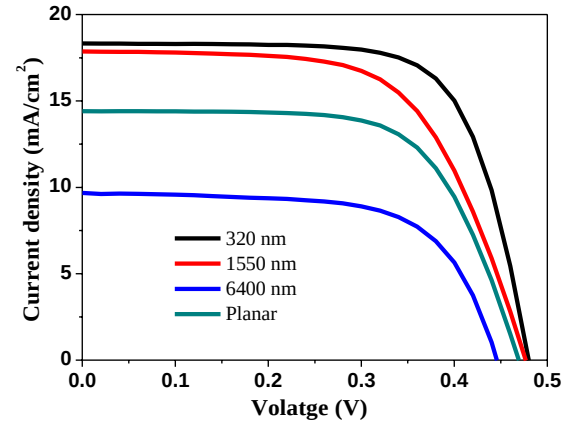


Fig. 3.3 Photocurrent density vs. voltage characteristics of planar cell and SiNW solar cells having different NW lengths under simulated AM1.5G illumination

Table 3.1. Solar cell parameters of SiNW array and planar

NW length (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)
0(planar)	14.41	0.47	0.65	4.45
320	18.32	0.48	0.7	6.16
1550	17.82	0.477	0.62	5.27
6400	9.67	0.445	0.65	2.98

increases up to a certain amount then it decreases with more increase in NW length. This has happened because of the fact that with increase of NW length surface related recombination starts to overcome the advantage

of excellent light trapping property of longer wavelengths. Fig. 3.3 shows the photo-current density vs voltage characteristics of SiNW array solar cells and planar solar cell under AM1.5G solar illumination (100 mW/cm^2). The solar cell parameters of these cells are presented in Table 3.1. From Table 3.1 it could be observed that SiNW array improves the cell performance compare to planar cell but with increase of NW length the cell performance degraded. For NW length up-to 1550 nm cell performance is still higher than that of planar cell. However, more increase in NW length degraded the cell performance and it goes below even that of planar cell for NW length 6400 nm.

3.4. Conclusion:

SiNW arrays of different NW length were fabricated by simple and low-cost MCEE technique. p-n junction was fabricated by spin-on-dopant technique followed by thermal diffusion of dopants. Current-voltage and EQE measurements shows that for SiNW arrays with smaller length of the NWs cell performance is higher than the planar cells while for longer NW length the cell performance degraded and even go below that for planar cell.

Reference:

1. M. Green, Prog. Photovoltaics, **17**, 183–189 (2009).
2. M. Dutta, L. Thirugnanam, P. V. Trinh, N. Fukata, ACS Nano, **9**, 6891–6899 (2015).
3. M. Dutta and N. Fukata, J. Nanosci. Nanotechnol. **14**, 1-8 (2014).
4. M. Dutta, L. Thirugnanam and N. Fukata, “Si nanowire solar cells: Principles, Device types, Future aspects and Challenges” in *Advances in Silicon Solar Cells*, edited by ShadiaIkhmayies Springer, Cham 2018), pp. 299-329.
5. S. Misra, L. Yu, M. Foldyna, P. R. I. Cabarrocas, Sol. Energ. Mat. Sol. C. **118**, 90–95 (2013).
6. M. Dutta and N. Fukata, Nano Energy, **11**, 219–225 (2015).
7. G. Jia, M. Steglich, I. Sill, F. Falk, Sol. Energ. Mat. Sol. C. **96**, 226–230 (2012).
8. T. Yoshida, M. Sakai, T. Tanabe, Mater. Trans. **45**, 2018–2022 (2004).
9. Z. Huang, N. Geyer, P. Werner, J. deBoor and U. Gösele, Adv. Mater. **23**, 285–308 (2011).
10. B. Hua, B. Wang, M. Yu, P. W. Leu and Z. Fan, NanoEnergy. **2**, 951–957 (2013).

Chapter 4

Growth of SiO₂ microparticles by using Stöber method: Effect of ammonia solution concentration and TEOS concentration

4.1. Introduction

The unique structural features of the micro particles have attracted a large attention since the last few decades. It is now being used for a large number of applications which include lithium ion batteries, catalysis, drug delivery [1], anti-reflective coating materials [2-3] and also for cosmetics [4-5]. Due to mobility and high mechanical strength [6-7] SiO₂ particles are also used for column packing, structural ceramics material ink additives etc. Beside these applications silicon micro particles are also used to fabricate microwires solar cell using nanosphere lithography techniques. The physical as well as the optical properties of the silica particles depend on the size of the particles. In order to get different sizes of the silica particles, various methods of preparations are adopted. Among the various methods used to prepare silica microspheres some are mechanical alloying method, micro emulsion method, hydrothermal synthesis method, precipitation, sol gel method and radiation synthesis method [8-11]. The solution gelation commonly known as sol gel method is preferred over all other methods as this method involves simple chemistry and involves low cost techniques. In the sol-gel method a classical method known as the Stöber method is used to produce monodisperse silica spheres [12, 13].

In this process silica precursor tetraethyl orthosilicate Si(OC₂H₅)₄ (abbreviation TEOS) is first reacted with water in an alcoholic medium typically ethanol in the presence of ammonia as a catalyst [14-15] and also with KCl electrolyte. It has been found that adding KCl could effectively increase the size of the silica particles.

Recently Xue Lei et al. [16] reported that using Stöber method monodisperse silica micro particles having a diameter of about 1-3µm could be obtained. Two different experiments were tried. In one the two solutions were allowed to react for 15 hours and after centrifugation and washing with ethanol it was found that the diameter of the micro particles was about 1µm. Further, they continued reaction in which a solution containing ethanol and TEOS was injected for 6 hours at 0.1-0.2ml/min in a solution containing KCl, ethanol, water and ammonia. This further the reaction was left for 5 hours. In this they synthesized micro particles of 2-3µm size.

4.2. Experiment

4.2.1. Materials

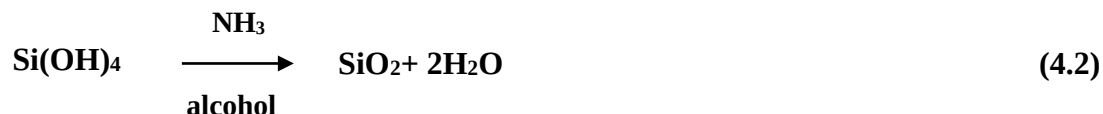
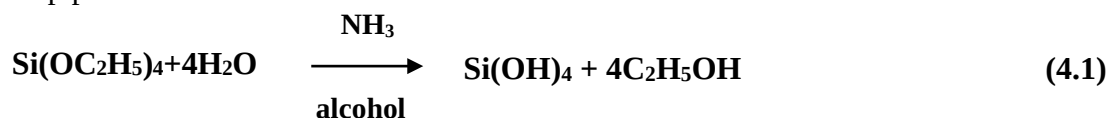
Tetraethyl orthosilicate (TEOS) was purchased from Sigma Aldrich. KCl and ethanol that has been used were purchased from the Merck life Science Private Limited. The ammonia solution (28-30%) for analysis was also purchased from Merck life Science Private Limited. All the other chemicals and the reagents were used as they were received without any sort of purification.

4.2.2. Preparation of the SiO₂ particles

Monodisperse SiO₂ micro particles were synthesized using simple modified Stöber method in an ethanol along with ammonia solution which is used as a catalyst. The reaction is carried out at room temperature in a 250ml beaker with mechanical stirring of about 200 rpm. Two solutions were made. Solution A was a mixture of KCl (15mg), ethanol (60ml), Water (7ml) and ammonia solution. Amount of ammonia solution was varied from 1.5ml, 3ml, 6ml and 9ml respectively. Solution B was a mixture of TEOS (3.5ml, 6.4ml) and Ethanol (38.5ml). The solution B was supplied to solution A using syringe pump. After the injection and further reaction, the micro particles were collected in a centrifuge tube and purified by centrifugation and washing by ethanol three times simultaneously. Finally, the micro particles were dried. The micro particles obtained finally are then weighed and used to make 30%, 15% and 7.5% solution using DMF. They are then spin coated on the cleaned n-type substrates.

4.2.3. Reaction mechanism

In this process, hydrolysis occurs in which ethoxy group present in the TEOS reacts with the water molecule and it produces an intermediate $[\text{Si}(\text{OC}_2\text{H}_5)_{4-x}(\text{OH})_x]$. Here hydroxyl group replaces the ethoxy groups. Ammonia is used as the basic catalyst to enhance the reaction. The reaction as shown in equation 1 will produce ethanol and a mixture of ethoxysilanols even $\text{Si}(\text{OH})_4$ which will then condense with either TEOS or other silanol and there is loss of alcohol or water. [15] This hydrolysis of the ethoxy group followed by the condensation process leads to crosslinking. All these reaction occurs in a single reaction vessel and so it is a one step process.



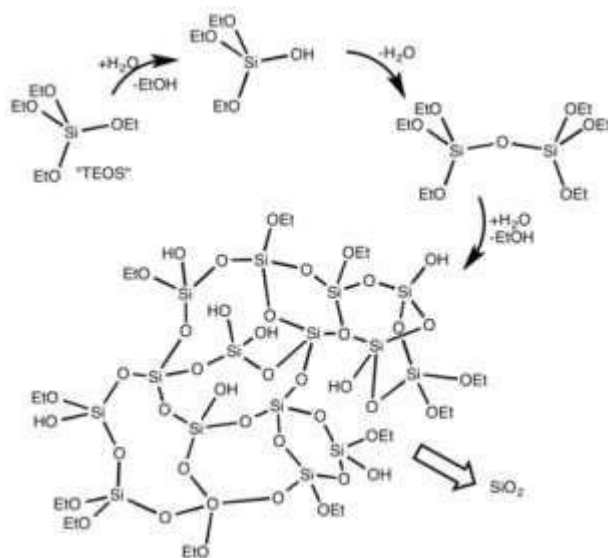


Fig. 4.1 Simplified representation of hydrolysis and condensation of TEOS in Stöber process

4.2.4. Characterization

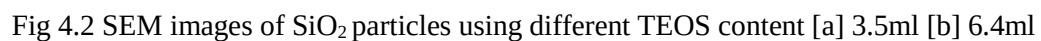
The size and the distribution of the silica micro particles synthesized are then viewed by an optical microscope. However high resolution images of the microspheres were taken using scanning electron microscope (SEM, Model: ZEIS EVO MA 10).

4.3. Results and Discussion

The morphological variation of the silica micro particles obtained from the experiment by varying the amount or concentration of the reactants are analyzed using SEM micrographs.

4.3.1 Effect of TEOS concentration on the Silica Particle Size

The concentration of TEOS also plays an effective role on the diameter of the silica particles. The concentration of TEOS is varied from 3.5 ml and 6.4ml respectively. It can be seen that there is a decrease in the average size of micro particles from 2.1 μ m to 1.8 μ m as the concentration of TEOS increases from 3.5ml to 6.4ml respectively. This is mainly because the initial concentration of TEOS is inversely proportional to the size of micro particles. That means higher the concentration there is smaller particles due to greater number of nucleation sites but with a greater spread of sizes.



Particle Size range (um)	Count
2.7-2.5	2
2.4-2.2	4
2.1-1.9	11
1.8-1.6	14
1.5-1.3	6
1.2-1.0	7
0.9-0.7	3

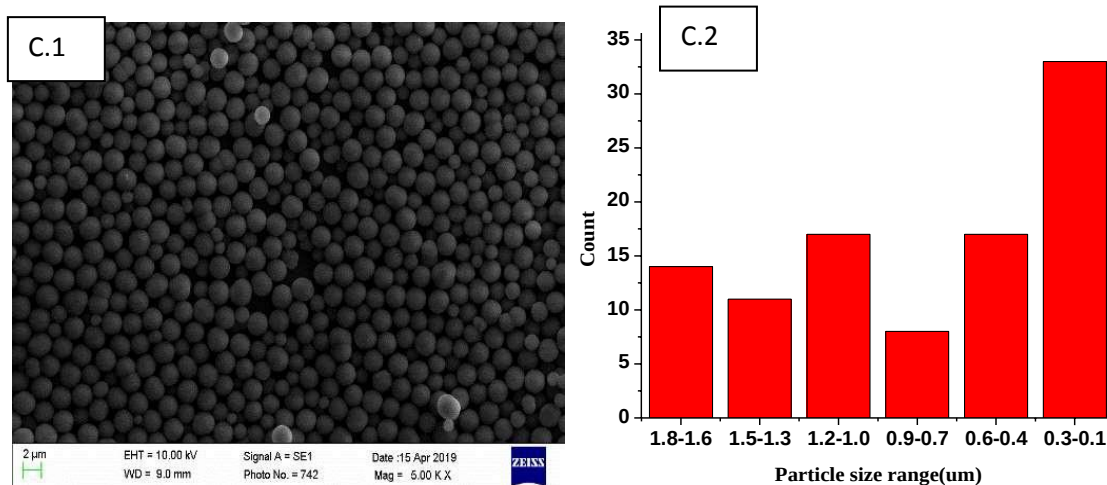


Fig 4.3 SEM images of SiO_2 microparticles (A1, B1, C1). Their corresponding histograms (A2, B2, C2) for particle sizes distribution using different ammonia content 3ml, 6ml and 9ml

Figure 4.3 shows that with the increase in ammonia content from 3ml to 9ml in the solution A there is a decrease in the diameter of the micro particles from $2.1\mu\text{m}$ to $0.3\mu\text{m}$. In this experiment the ammonia is mainly used as a catalyst and water reagent provider. With the increase in ammonia concentration the quantity of the silica nuclei in the initial nucleation increases resulting in decrease in particle size.

4. Conclusion

Monodisperse silica microspheres are synthesized using modified Stöber method. The diameter of the silica micro particles that are obtained by supplying TEOS continuously using syringe pump is much larger than traditional method. The amount of TEOS concentration as well as ammonia concentration also plays an important role in particle size.

Reference

1. A. Paci, L. Mercier, P. Bourget, J. Pharmaceutical Biomedical Analysis **30**, 1603–1610 (2003).
2. T. I. Suratwala, M. L. Hanna, E. L. Miller, et al., Journal of Non-Crystalline Solids **316**, 349–363 (2003)
3. X. Li, X. Du, J. He, Langmuir **26**, 13528–13534 (2010).
4. J. Dutta, H. Hofmann, R. Houriet, et al., AIChE Journal **43**, 2610–2615 (1997).
5. A. Jaroenworarluck, W. Sunsaneeyametha, N. Kosachan, et al., Surface and Interface Analysis **38**, 473–477 (2006).
6. Q. Lihai, L. Yuanfang, J. Zhixin, J. Demin. Functional Materials, 2013, **44** (5): 722-726
7. Z. Xiaoyu, Z. Qiuyu, W. Xiaoqiang, et al. Chemical Engineering, 2010, **38**(3): 72-75.
8. Z. Saifen, W. Zhouan. Shanghai Chemical Industry [J]. 2001, **8**(1):22-25.
9. M. F, Blanco A, Miguez H, et al. Colloids and Surfaces A Physicochemical and Engineering Aspects, 2002, **202**(2): 281-290
10. M. Gang, C. Ping, R. Nan. Chemical Journal [J]. 2008, **29**(12):2511-2515.
11. Park S K, Kim K D, Kim H T. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2002, **197**(1): 7-17.
12. W. Stöber, & A. Fink, J. Colloid Interf. Sci. **26**, 62–69 (1968)
13. L. Xue, B. Yu, H. Cong, C. Tian, Y. Wang, Q. Wang, & C. Liu, Integr. Ferroelectr. **154**, 142–146 (2014)
14. Stöber, Werner; Fink, Arthur; Bohn, Ernst (January 1968). " Journal of Colloid and Interface Science. **26** (1): 62–69.
15. V. Blaaderen, A; V. Geest, J; Vrij, A (December 1992). Journal of Colloid and Interface Science. **154** (2): 481–501.

16. Lei, X., Yu, B., Cong, H.-L., Tian, C., Wang, Y.-Z., Wang, Q.-B., & Liu, C.-K. (2014). Integrated Ferroelectrics, **154**(1), 142–146.

Chapter 5

Fabrication of Silicon Microwire array solar cells by using nanosphere lithography in addition to MCEE technique and its advantage over Silicon Nanowire array solar cells

5.1 Introduction:

Silicon nanowires (SiNWs) have been attracting a great deal of interest as a promising material for solar energy conversion to respond to the high demand for alternative renewable clean energy. High surface and interface recombination of photogenerated charge carriers and difficulties in fabricating high quality radial junction outweigh the advantages of using SiNWs. Promising diffusion process used to make radial junction in SiNWs most of the time results uncontrolled junction depths and even completely depleted SiNWs [1, 2]. Thus it seems to be difficult to fabricate controlled radial junction SiNW arrays by diffusion process and exploit the benefits of core-shell structure radial junctions. Use of CVD technique to deposit opposite polarity shell layer to fabricate radial junction in core-shell morphology is challenging in view of quality, crystallinity and cost [3, 4]. Again the large surface area of radial junctions results in high surface and interface recombination of photogenerated charge carriers that restrict the efficiency [4, 5]. Also the problems in controlling the position, spacing and diameter have been an issue of time consuming and costly top-down techniques.

In this work we have tried to resolve these issues by using Si microwire (SiMW) arrays fabricated by simple and low-cost nanosphere lithography technique together with MCEE technique [6, 7]. p-n junction has been achieved by spin-on dopant technique followed by thermal diffusion.

5.2 Experimental:

5.2.1 Procedure

Si substrates were cleaned by sonication in acetone, IPA, DI water then cleaned in a boiled solution of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:5$ for 1 h to make the surface hydrophilic. After rinsing by water and subsequent drying by air, these substrates were spin coated by SiO_2 microparticle solution in DMF and dried under natural environment to form self assembled monolayer (in closed pack form) of SiO_2 microparticles. These microparticle coated substrates are then transferred in reactive ion etching (RIE) chamber to form non closed pack structured. An Ag layer was evaporated over this non closed pack SiO_2 template. Ag film goes through the spacing among the microparticles and touches the Si surface underneath. After Ag evaporation the SiO_2 template was removed from the Si surface by a short ultrasonication for 2 min. A periodic microhole array

Ag film was formed on Si surface. This Ag film was used as a catalyst to etch the Si surface in HF/H₂O₂ solution for specific time. So the pattern of the Ag film was transferred on the Si surface. After etching the substrates were thoroughly rinsed with DI water. The Ag films were removed by HNO₃ and again thoroughly washed by DI water. The MW arrays fabricated by this etching process were analyzed by SEM. Formation of p-n junction over these MWs and electrode deposition are same as given in the experimental section of chapter 3

5.2.2 Characterization:

The instrumental facilities used for morphological and electrical characterizations are same as mentioned in chapter 3 and 4

5.3 Results and Discussion:

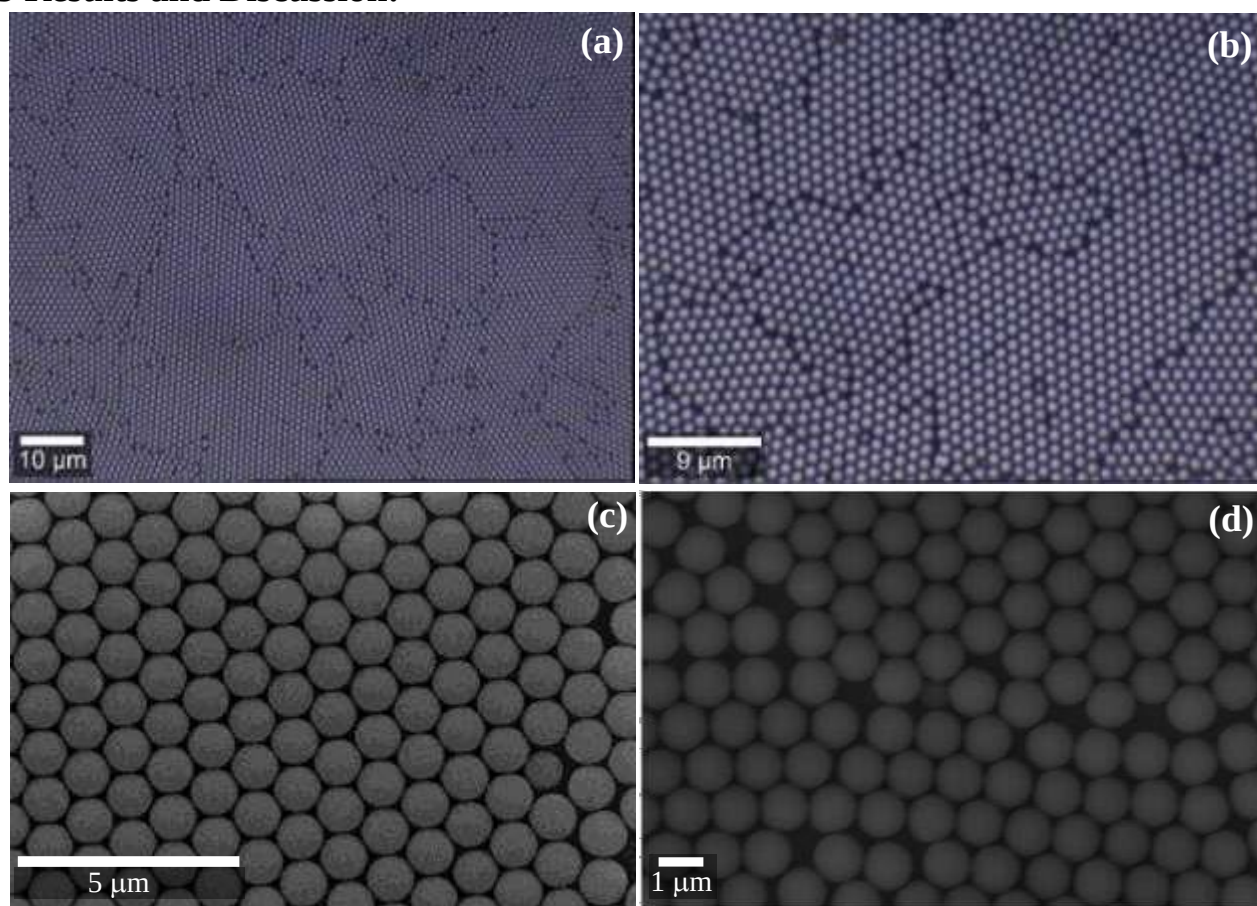


Fig. 5.1 SEM images of self assembled single monolayer (closed-pack) of SiO₂

Fig. 5.1 shows the self assembled monolayer of microparticles on the Si substrate that was obtained by spin coating of SiO₂ microparticles dispersed in DMF. Analysis of the SEM images shows that the average diameter of these microparticles is around 1 μm. After formation of self assembled single monolayer reactive ion etching (RIE) was performed to reduce the diameter of microparticles by 120 nm as shown in Fig 5.2. Fig

53 shows the SEM images of the microwires fabricated after etching in HF/H₂O₂ solution. Fig. 5.4 shows the comparison of the current density vs. voltage characteristics of SiMW array solar cell and SiNW array solar cell prepared under same condition illuminated by AM1.5G solar simulator. The main improvement in terms of J_{SC} has been observed in SiMW solar cell. However, very slight improvement could be seen in Voc and FF. These improvements could be attributed to the formation of radial junction within SiMW. Table 5.1 shows the solar cell parameters of these cells.

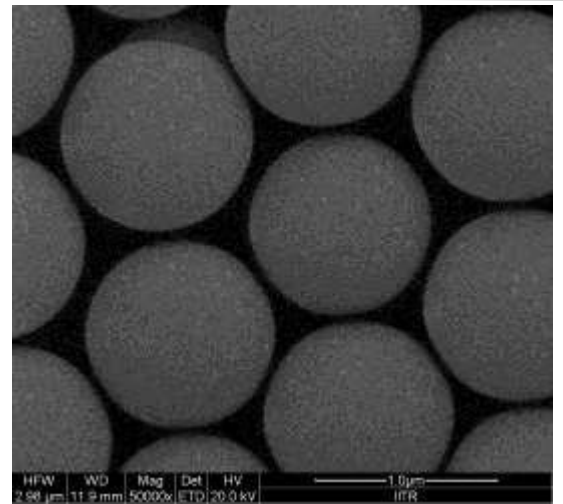


Fig. 5.2 SEM image of single monolayer of SiO₂ microparticles after RIE.

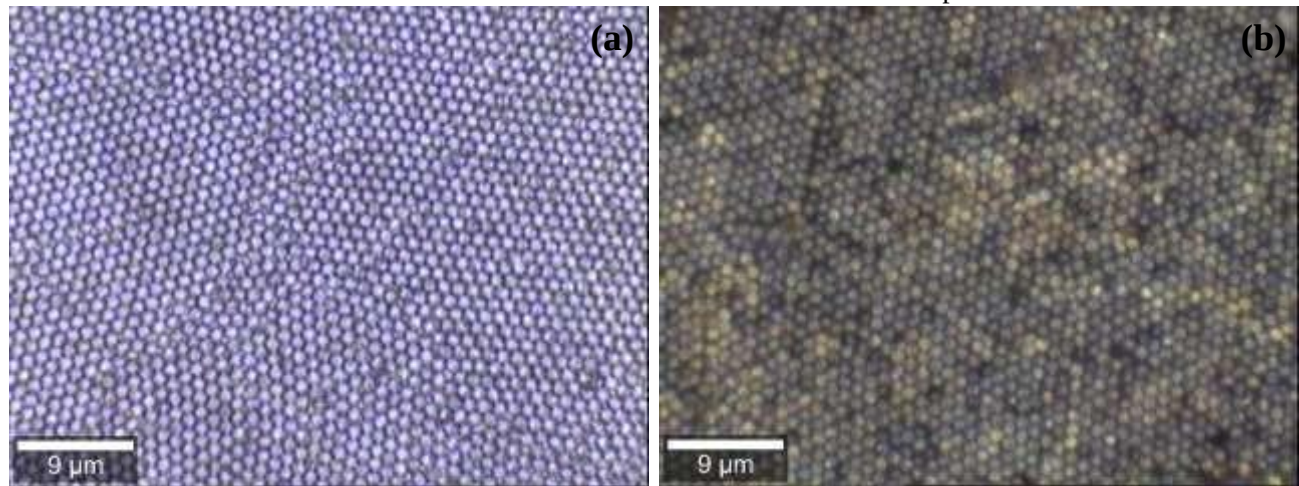


Fig. 5.3 Micrographs (Top view) of the SiMW arrays formed after etching in HF/H₂O₂ solution.

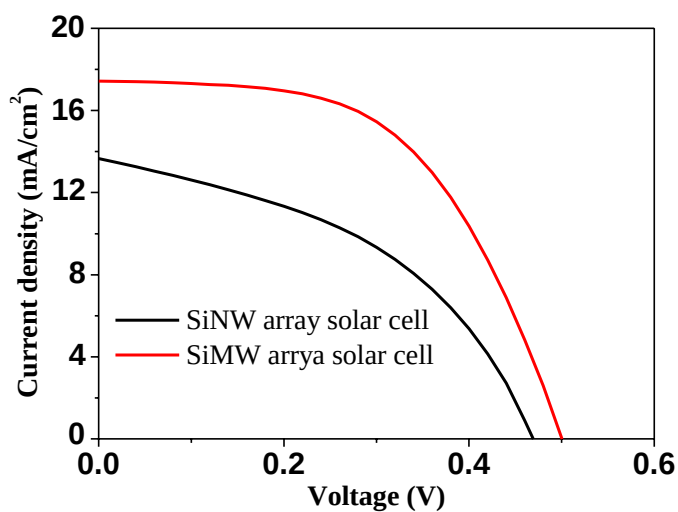


Fig. 5.4 Current density-Voltage Characteristic of SiMW and SiNW array solar cells.

Table 5. 1. Solar cell parameters of SiMW array and SiNW array solar cells

Solar cell	J _{SC} (mA/cm ²)	V _{oc} (V)	FF	η (%)
SiMW arrays	17.44	0.5	0.55	4.8
SiNW array	13.66	0.47	0.44	2.8

5.4 Conclusion:

SiMW array have been prepared by nanosphere lithography technique in addition to the MCEE technique. SiMW arrays has been characterize by SEM. SiMW array solar cell has been prepared by spin-on-dopant technique followed by thermal diffusion. SiMW array solar cell shows better performance compare to SiNW array solar cell prepared under identical condition. The reason for this could be attributed to the formation of radial junction inside the SiMWs.

Reference:

1. D. Kumar, S. K. Srivastava, P. K. Singh, M. Husain and V. Kumar, Sol. Energ. Mat. Sol. Cells **95**, 215–218 (2011).
2. F. Khan, S. –H. Baek and J. H. Kim, Solar Energy **137**, 122–128 (2016).
3. M. Dutta, L. Thirugnanam, P. V. Trinh and N. Fukata, ACS Nano **9**, 6891–6899 (2015).
4. G. Jia, M. Steglich, I. Sill and F. Falk, Sol. Energ. Mat. Sol. Cells, **96**, 226-230 (2012).
5. M. Dutta and N. Fukata, Nano Energy **11**, 219–225 (2015).
6. K. Peng, M. Zhang, A. Lu, N.-B. Wong, R. Zhang, and S.-T. Lee, Appl. Phys. Lett. **90**, 163123 (2007).
7. Y. Lu, H. Xiong, X. C. Jiang, and Y. N. Xia, J. Am. Chem. Soc. **125**, 12724 (2003).

Conclusion

SiNW array solar cells are promising alternative for low cost solar cells compared to commercial planar Si solar cells. SiNW arrays provide short carrier transportation length and decoupling of direction of the charge carrier transportation and absorption of light when radial junction could be established. This radial junction solar cells could give efficiency much higher than present commercial Si solar cells at relatively low cost. However, difficulties in realizing radial junction restricts the achievement of such kind of higher efficiencies. This dissertation work has been designed to understand the problem behind this realization of radial junction.

SiNW arrays has been fabricated using simple low-cost and quite effective MCEE technique and p-n junction are established by spin-on-dopant technique followed by thermal diffusion. It has been found that thermal diffusion process could fully deplete the small diameter SiNWs, so very high efficiency could not be achieved as radial junction couldn't be realized by this method. However, through this work it has been established that with increase of NW length performance of SiNW array solar cells are degraded even though longer NW arrays show excellent light trapping. Nevertheless, short SiNW arrays even shows higher performance than planar Si solar cells produced under identical conditions.

It has been observed during our work that increase in diameter of the Si wires could resolve the problem. So higher diameter Si wires (i.e. SiMWs) has been fabricated by simple low-cost nanosphere lithography technique in addition to MCEE technique. To carry out the nanosphere lithography work SiO₂ microparticles has been synthesized using modified Stober method and effects of precursors and catalyst concentrations are studied. In next step using SiO₂ microparticles around 1 μ m diameter has been used for the production of self-assembled single layer non-closed packed SiO₂ template to carry out nanosphere lithography process. After fabrication of SiMW arrays their morphology has been studied and SiMW array solar cell has been produced under identical condition as that SiNW array solar cells. Comparison of SiMW array and SiNW array solar cell performance shows that SiMW array are much more efficient in terms of higher J_{sc} values and slight larger V_{oc} and FF.

Future Work

This dissertation work shows that more work yet to be done in the field of SiMWs. Still in Si MW the problem of surface recombination persists and compare to SiNW arrays. SiMW array light trapping capability is less. So the reflectance should be high. My future work should be directed towards the optimization of SiMW arrays for solar cells by fabricating homogeneous and continuous arrays on wafer scale and minimizing surface defects by using several surface passivation methods. Also different light trapping mechanism has to be investigated to enhance the absorption of light inside this MW arrays.